

# **Weekend/Weekday Ozone Study in the South Coast Air Basin**

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Weekend Ozone Effect Workshop  
Sacramento, CA  
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# **OVERVIEW**

- 1. Summary of Findings  
Desert Research Institute  
Sonoma Technology, Inc.**
- 2. Conclusions and Recommendations**

Hypotheses	Significance	Confidence Level
1. NOx reduction		
2. NOx timing		
3. Pollutant carryover near the ground		
4. Pollutant carryover from aloft		
5. Increased weekend VOC emissions		
6. Increased photolysis due to decreased PM		

# Confidence Level

- **High confidence:** There is high certainty in the data or data analysis approach or the conclusion is supported by more than one independent analysis approach, each of which has low to moderate uncertainties.
- **Medium confidence:** There is moderate uncertainty in the data or data analysis approach and independent analysis approaches were not applied.
- **Low confidence:** There is large uncertainty in the data or data analysis approach and independent analysis approaches were not applied or were contradictory.

# **SUMMARY OF FINDINGS**

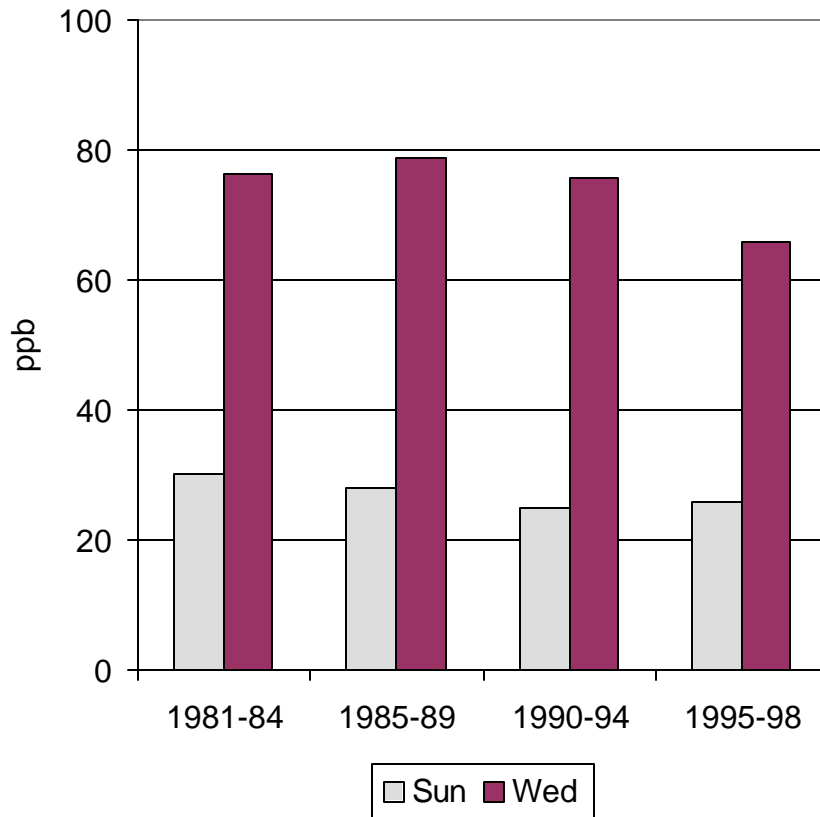
**Desert Research Institute**

## Hypotheses for why ozone is higher on weekends

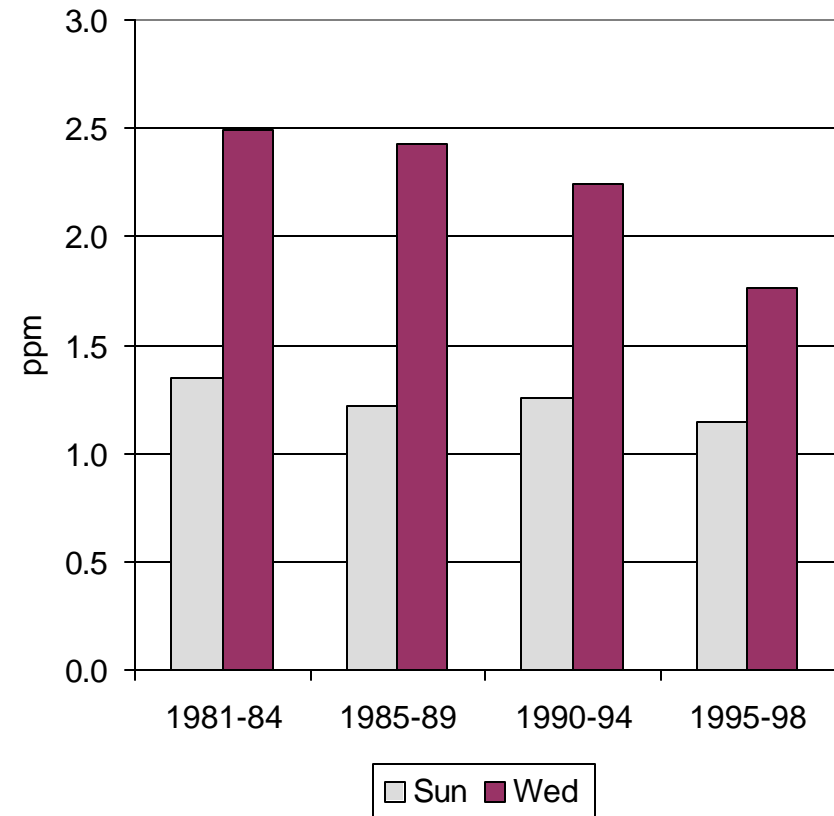
- **NO<sub>x</sub> reduction.** Lower concentrations of NO<sub>x</sub> on weekend mornings leads to higher ozone concentrations on weekends because the accumulation of ozone begins earlier on weekends due to less titration of ozone with NO and because of the higher rate of ozone accumulation due to higher VOC/NO<sub>x</sub> ratios.

# Mean 7-8 a.m. Nitric Oxide and Carbon Monoxide Mean of 12 sites in SoCAB, 1981-98

NO (ppb)



CO (ppm)



0.39

0.36

0.33

0.39

Sun/Wed

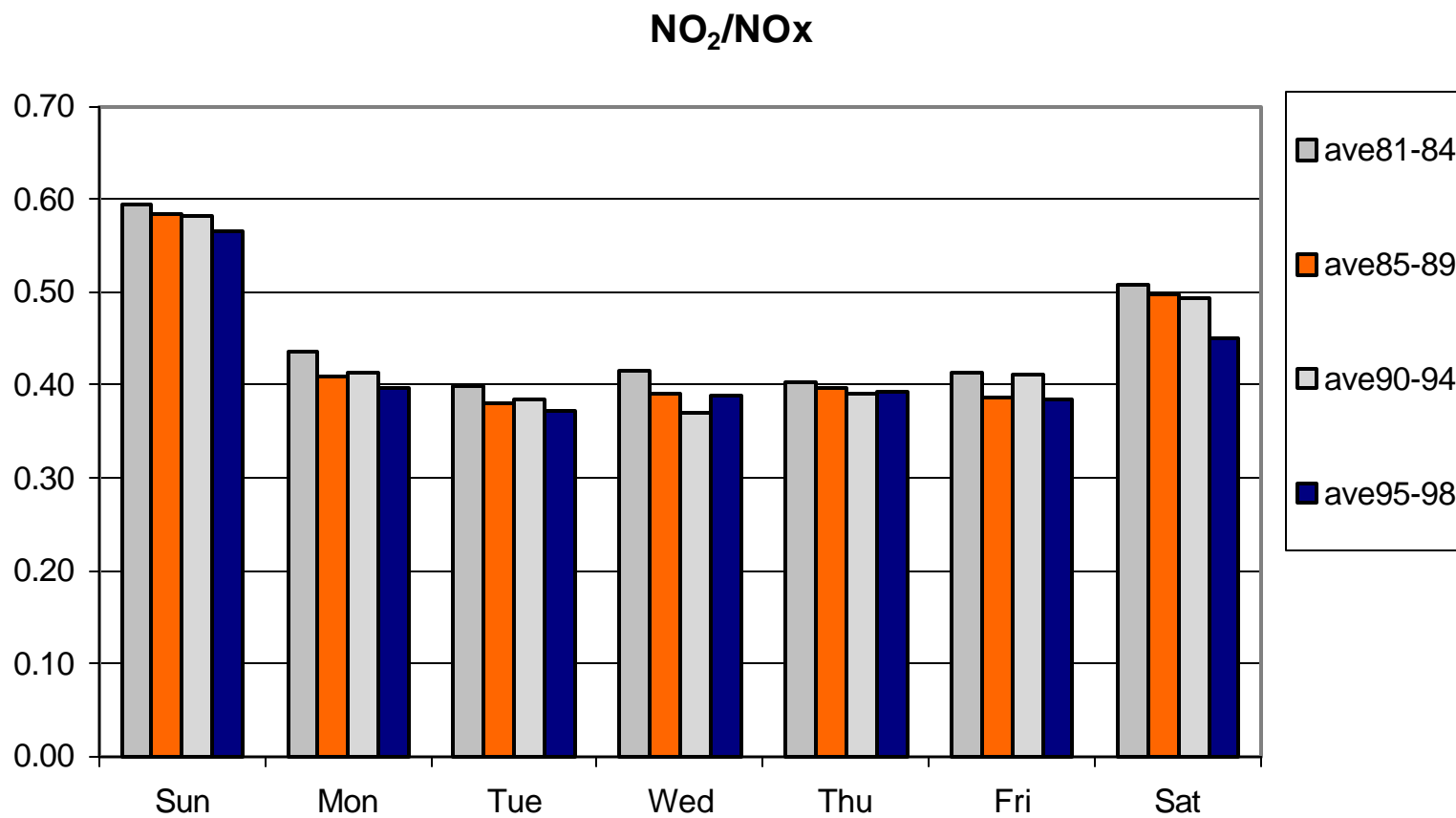
0.54

0.50

0.56

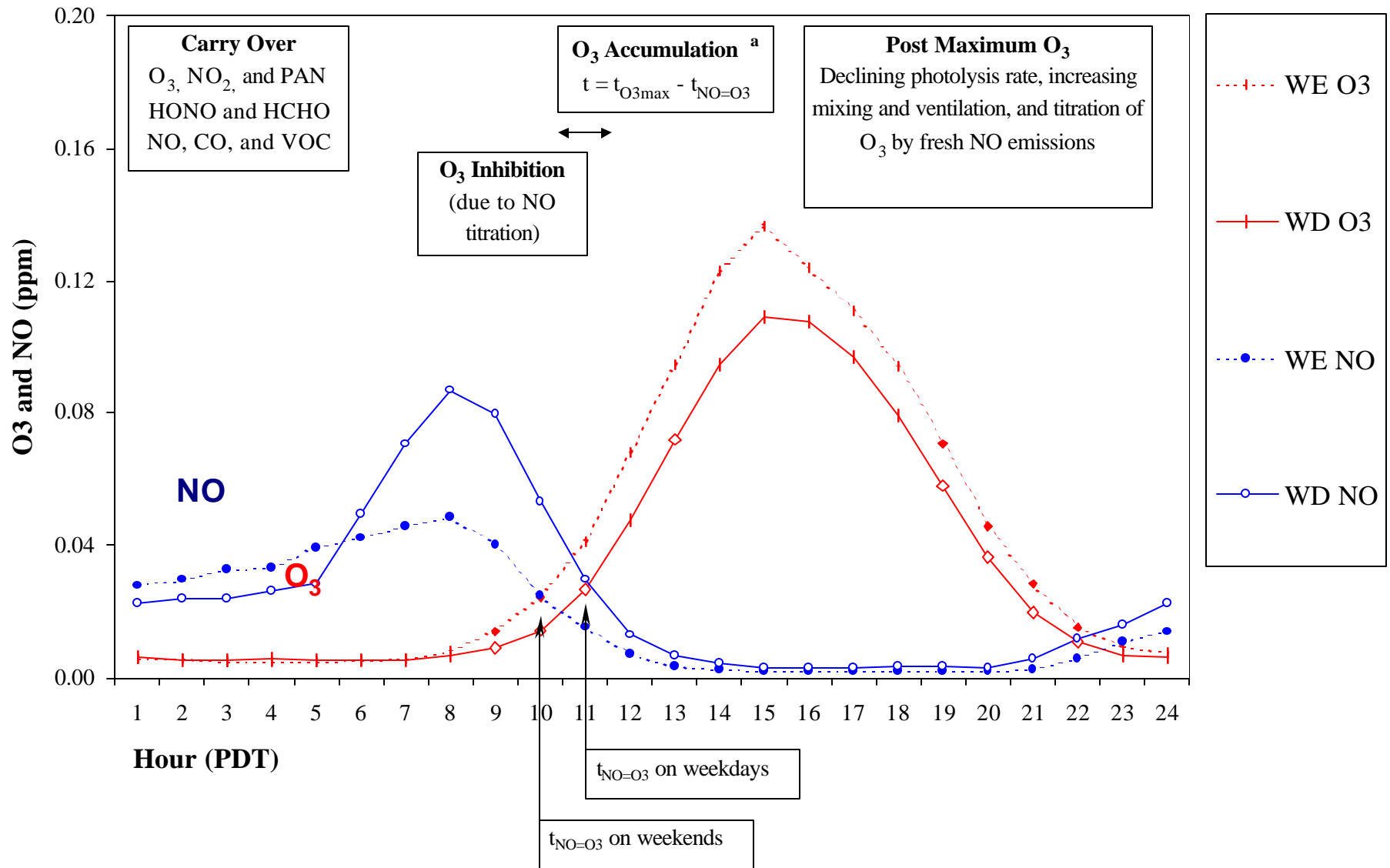
0.65

## Twelve-Site Average NO<sub>2</sub>/NO<sub>x</sub> Ratios at 7-8 a.m. (PDT) by Day of the Week

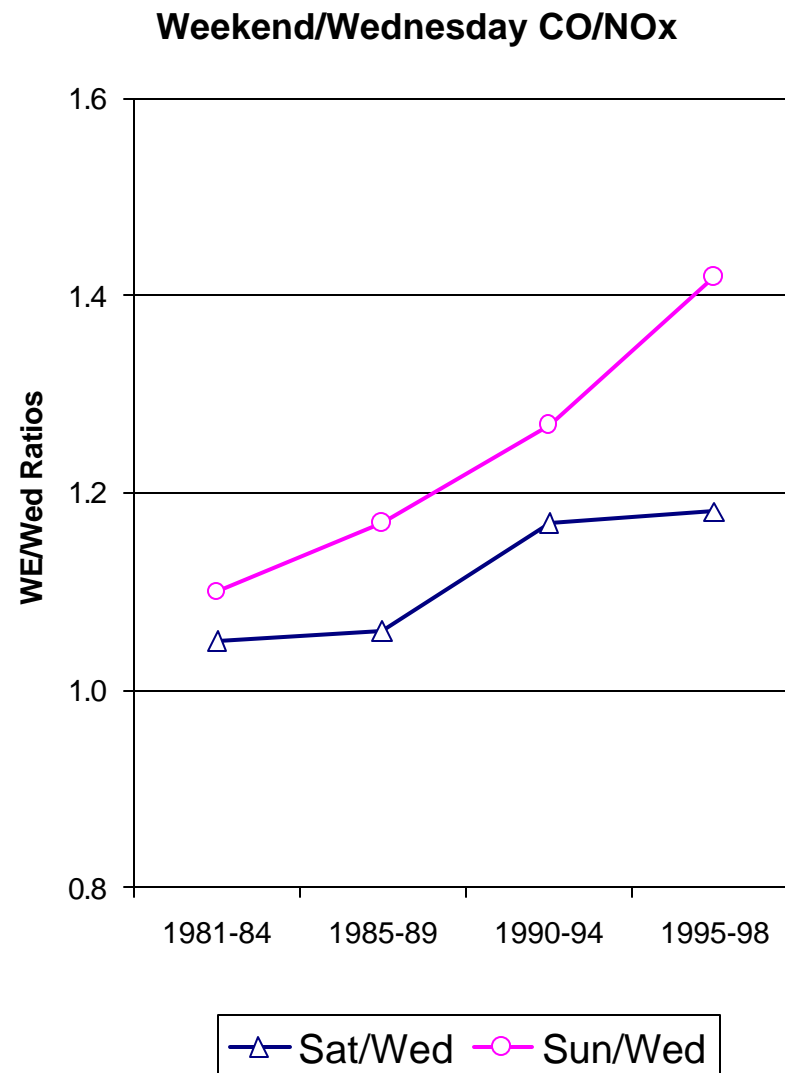
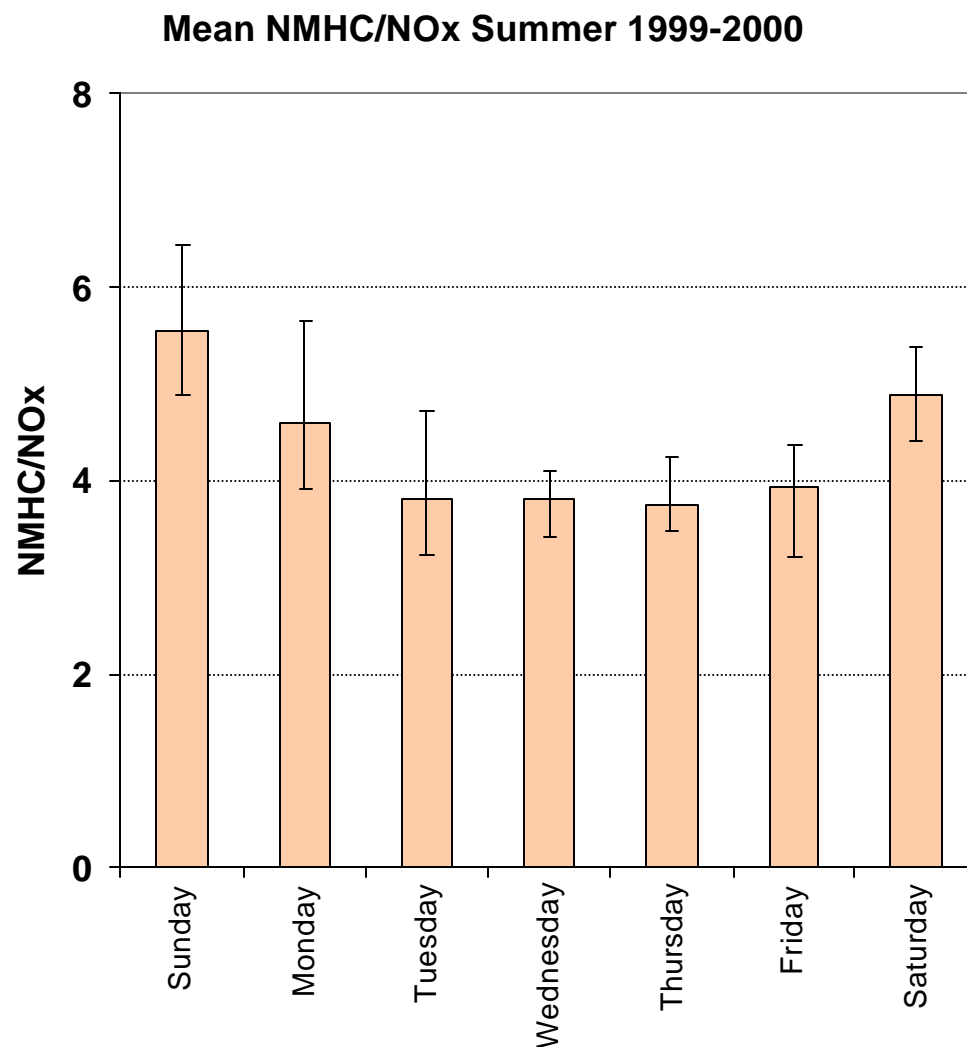




# Azusa, Summer 1995



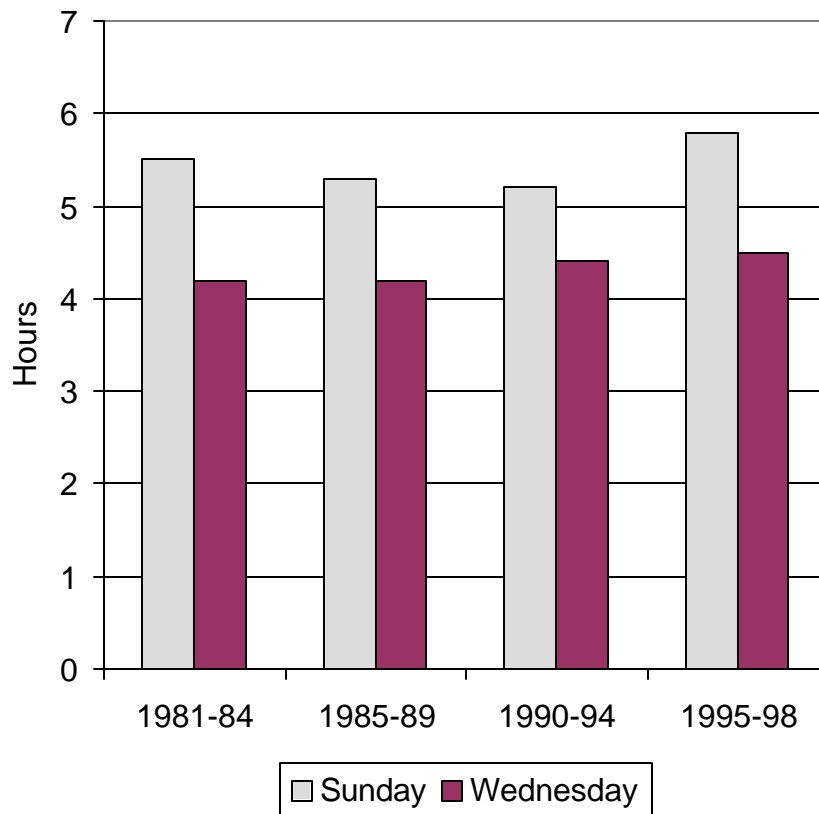
# Weekday Variations in NMHC/NOx



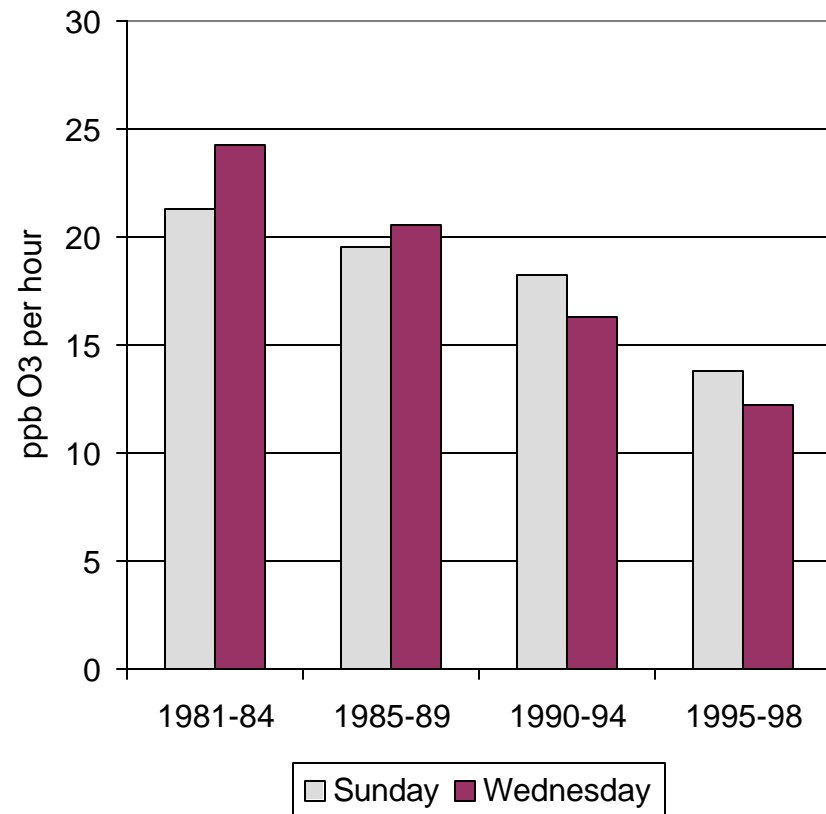
Whiskers are one standard deviation of mean ratios at four sites.

# Duration and Rate of Ozone Accumulation Mean of 12 sites in SoCAB, 1981-98

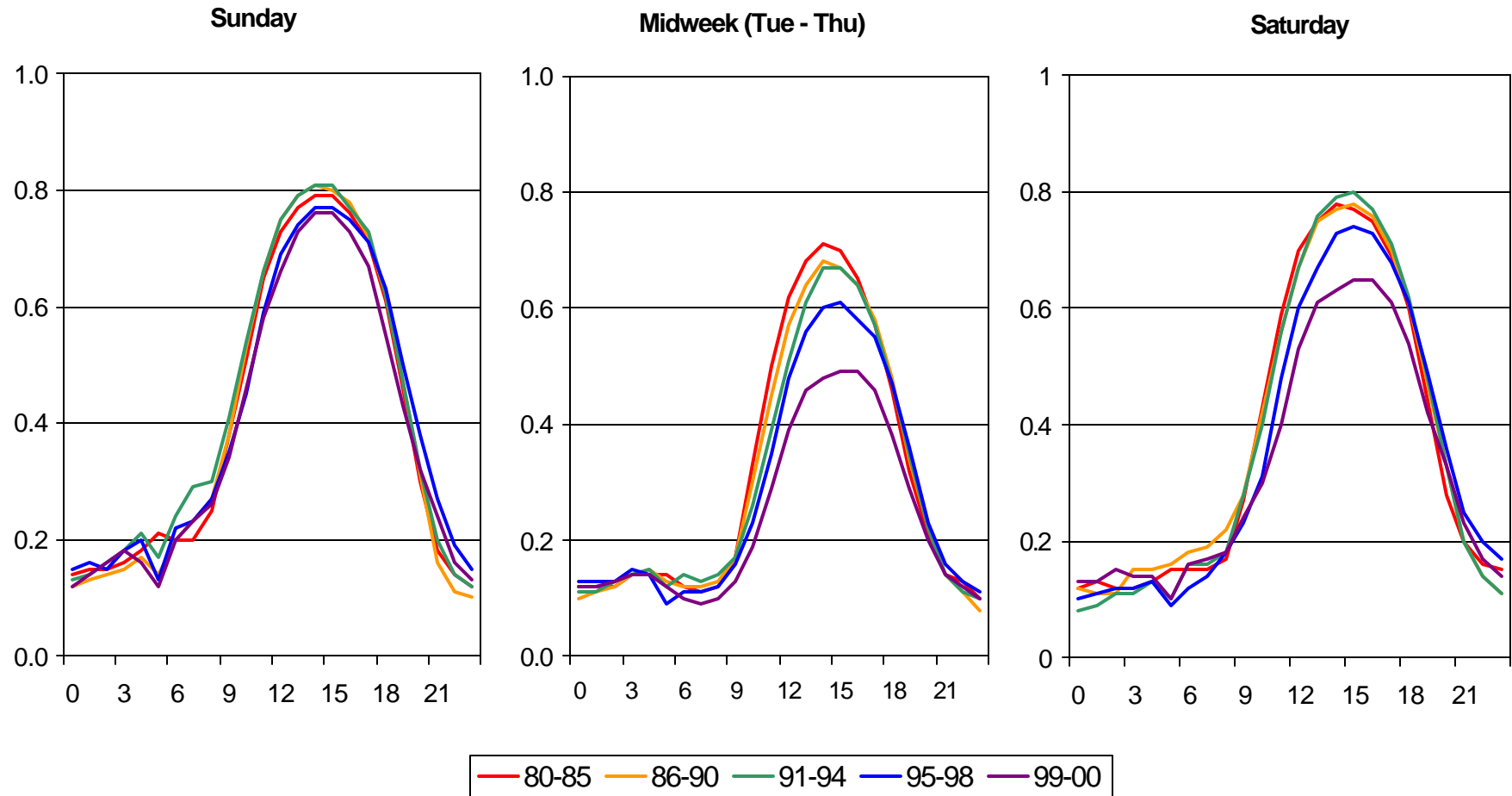
Duration (hours)



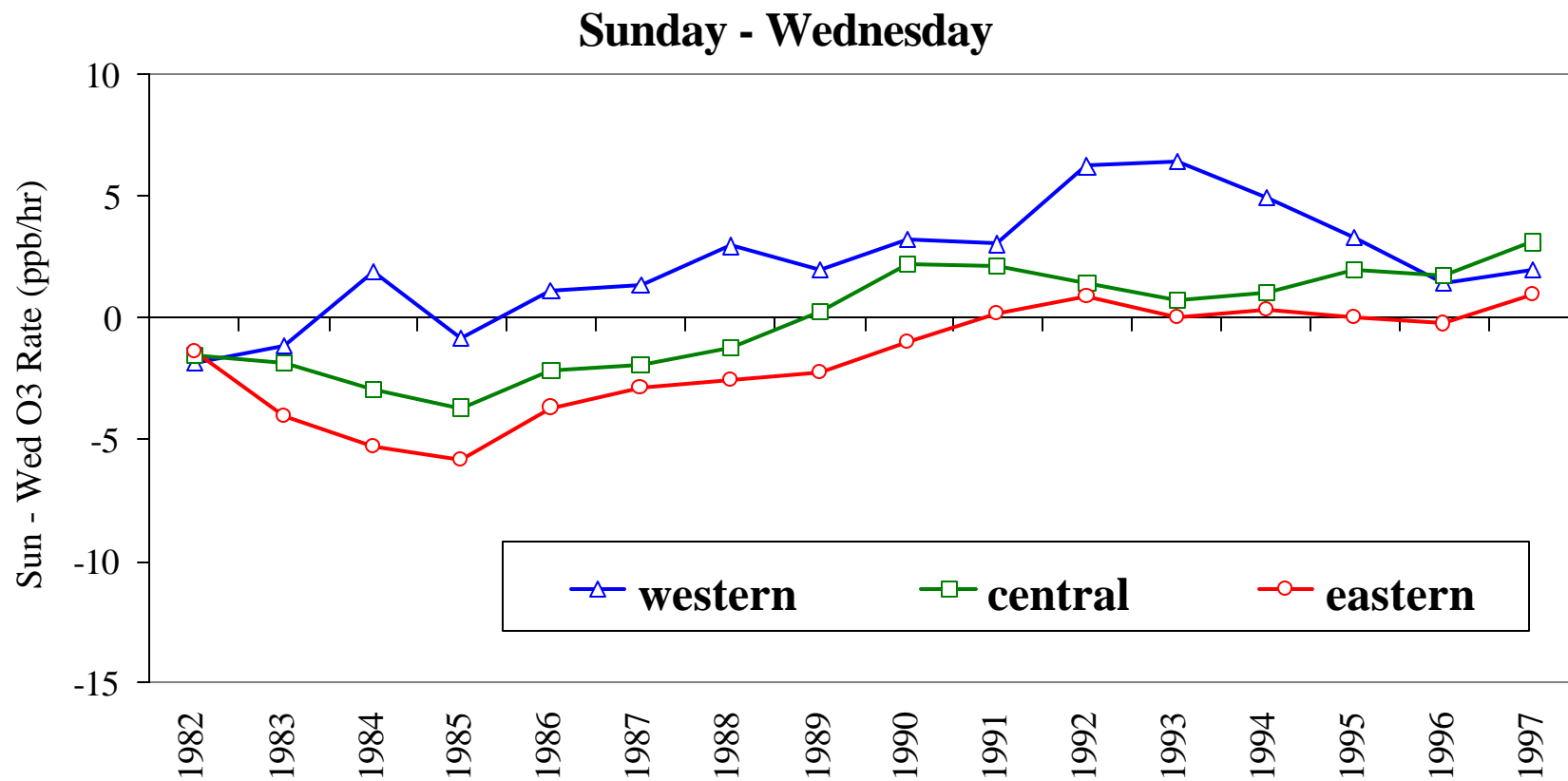
Rate (ppb/hour)



# Ratio of Peak Ozone to Potential Ozone (O<sub>3</sub> + NO<sub>x</sub>) 1980 to 2000

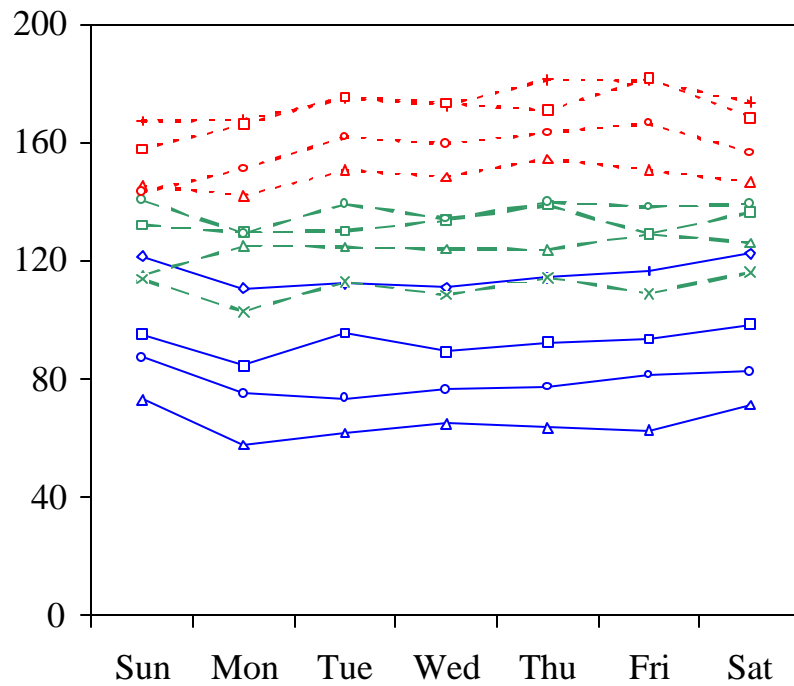


## WE/WD Differences in Ozone Accumulation Rates in the SoCAB 3-Year Running Averages from 1982 to 1997

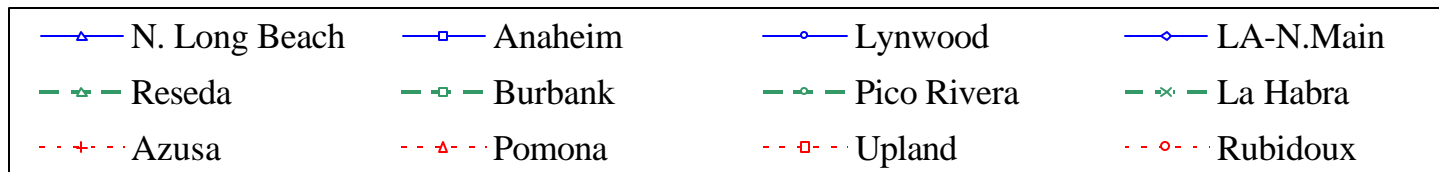
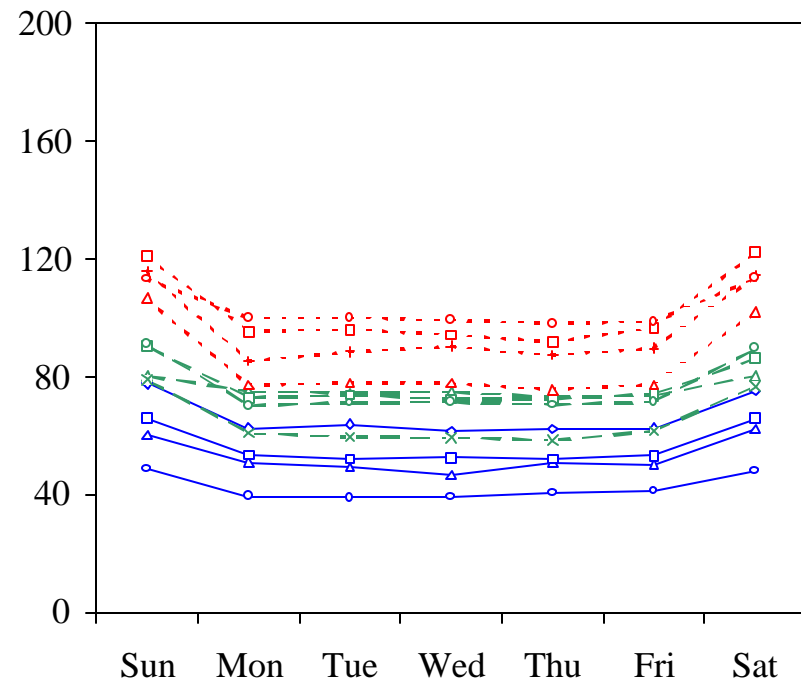


# Weekday Variation in Peak Ozone

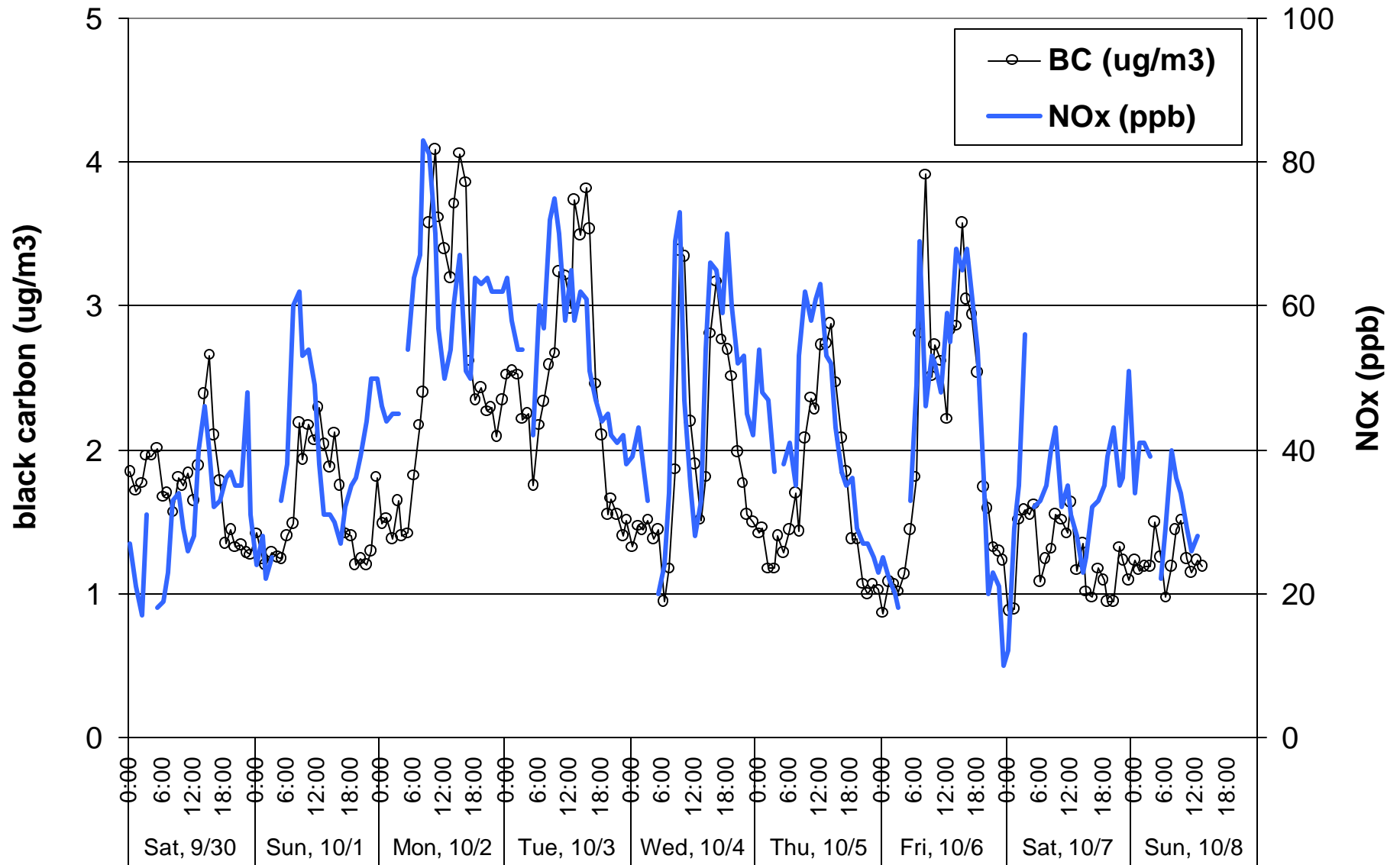
1981-84



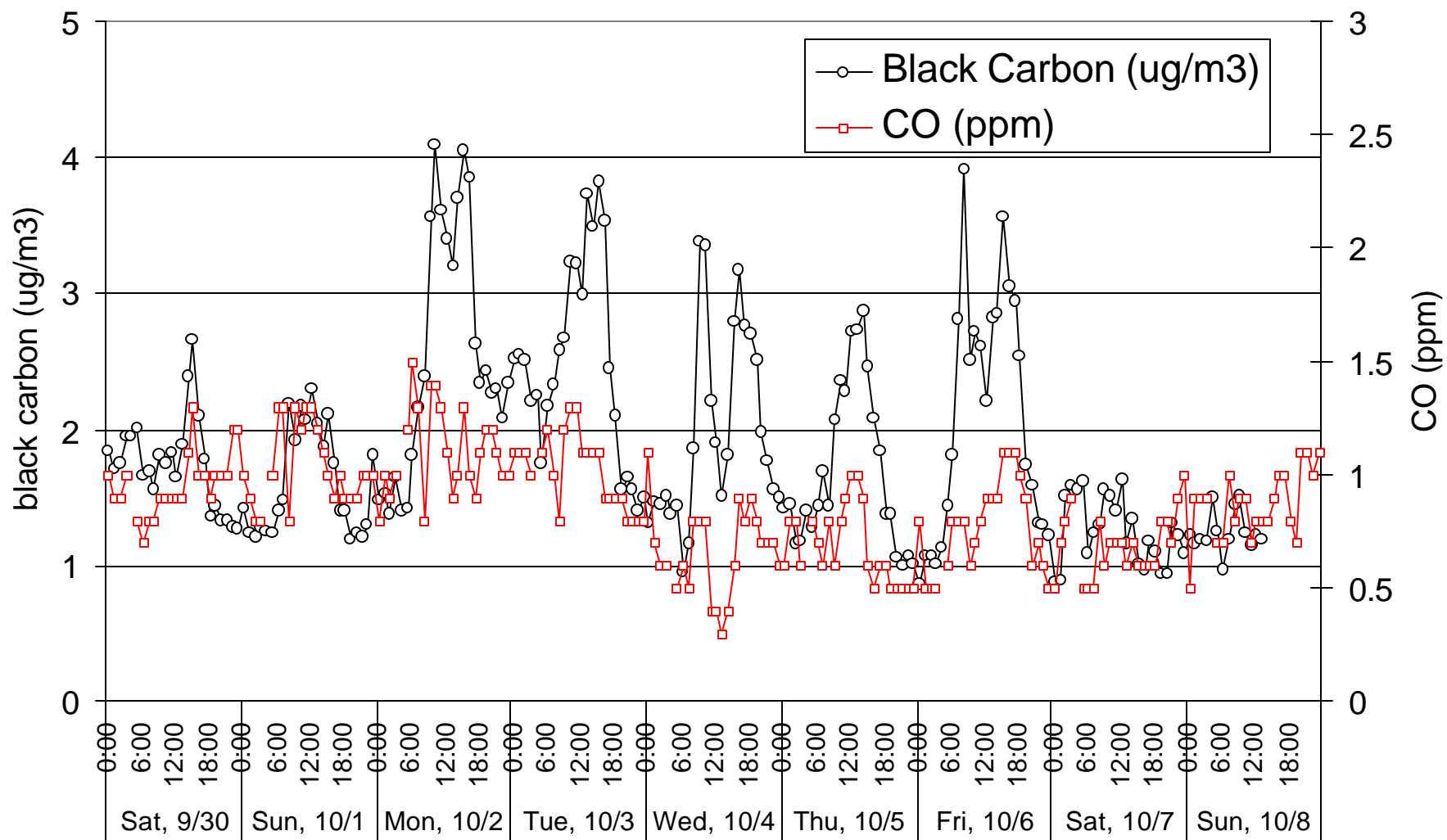
1995-98



## Black Carbon and NOx at Azusa, 9/30/00 to 10/8/00

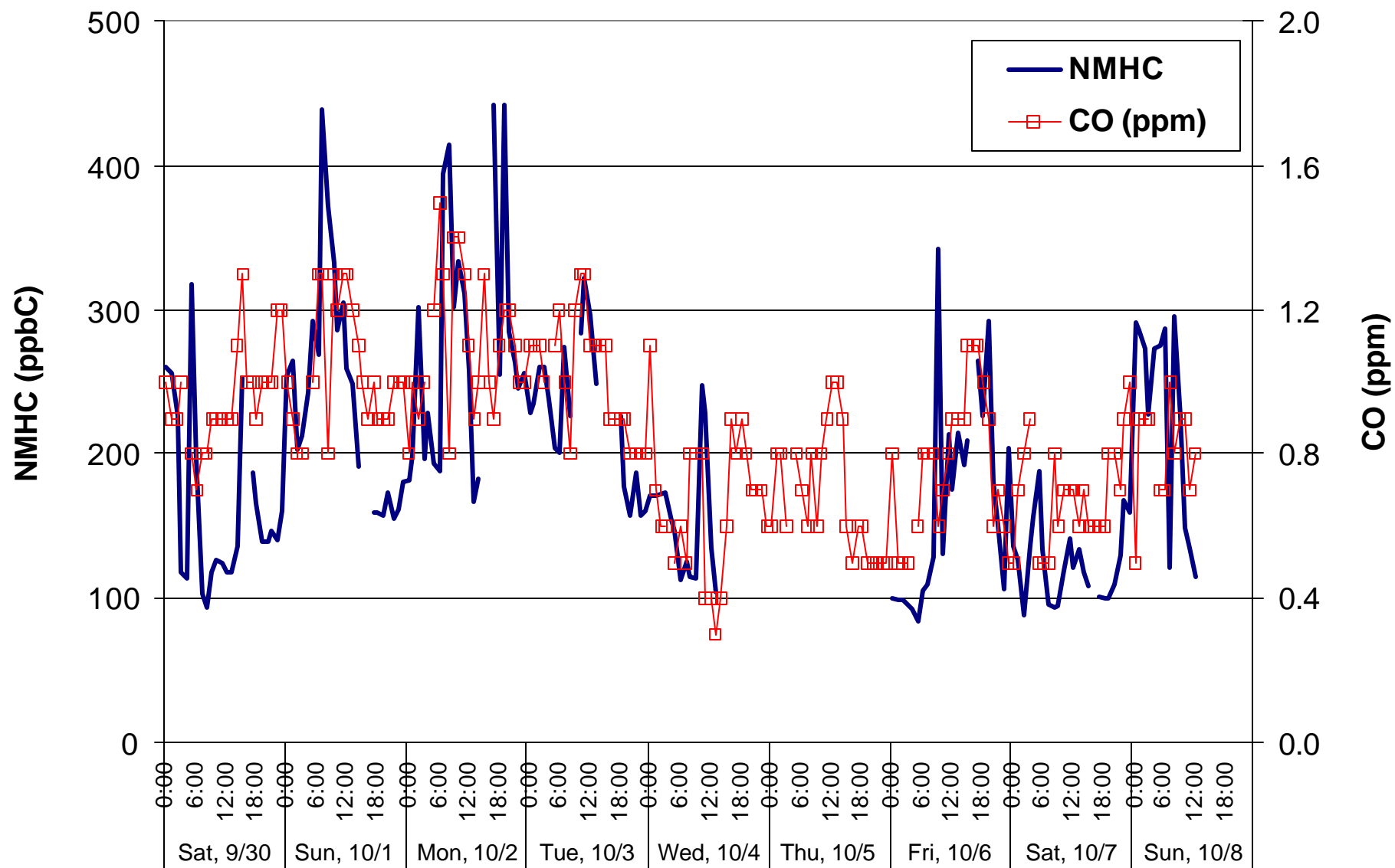


## CO and Black Carbon at Azusa, 9/30/00 to 10/8/00

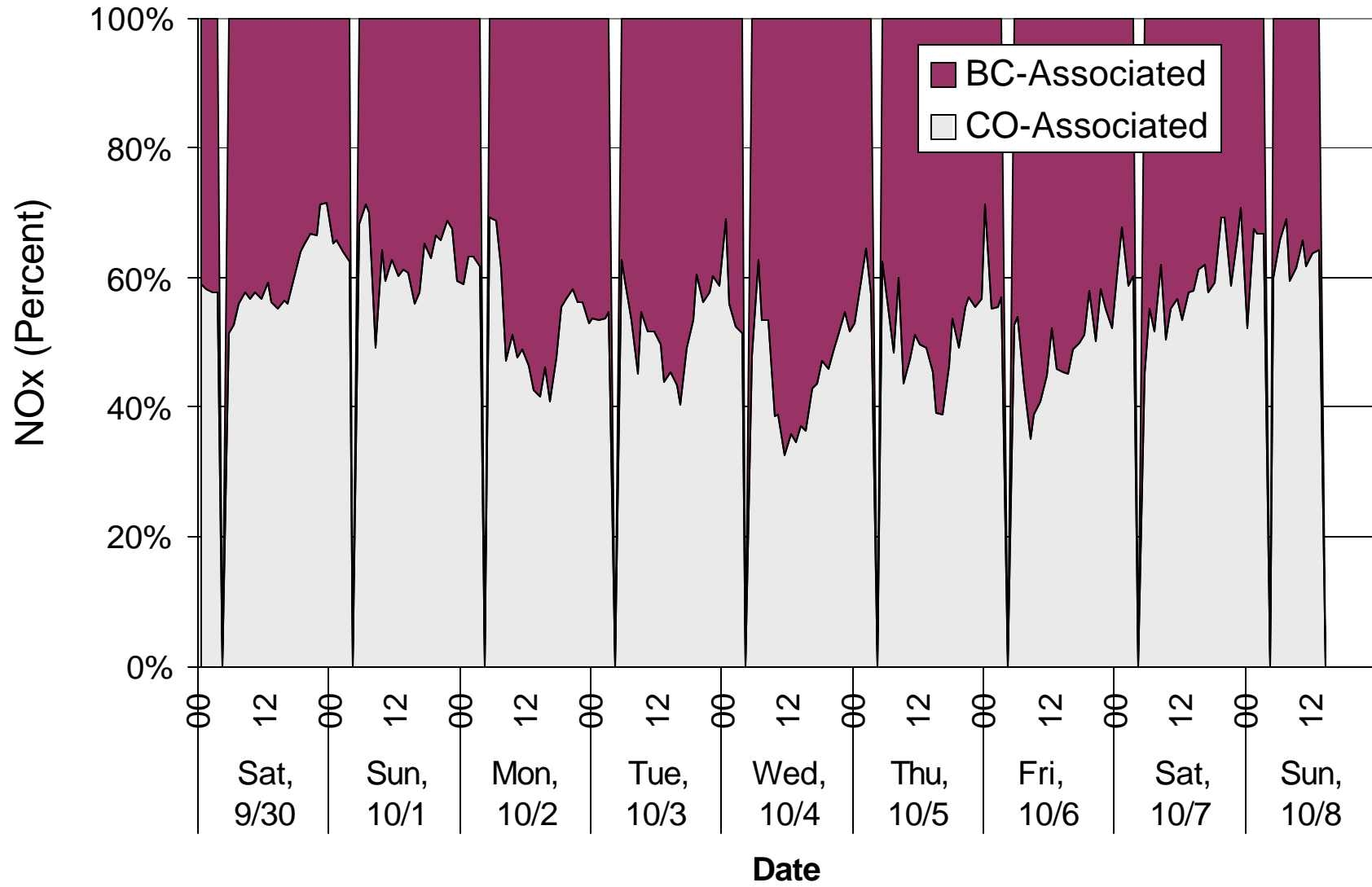




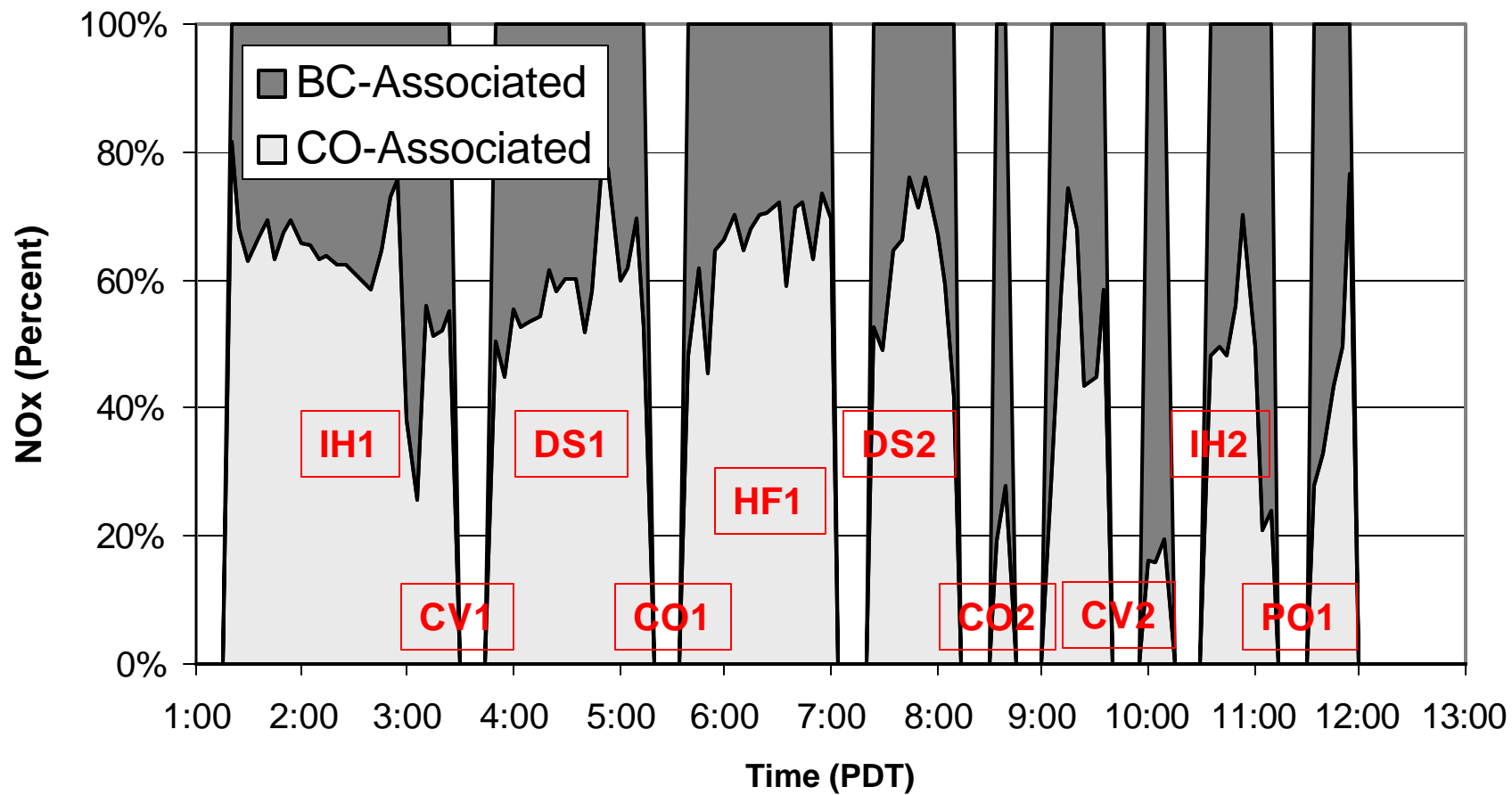
# NMHC and CO at Azusa, 9/30/00 to 10/8/00



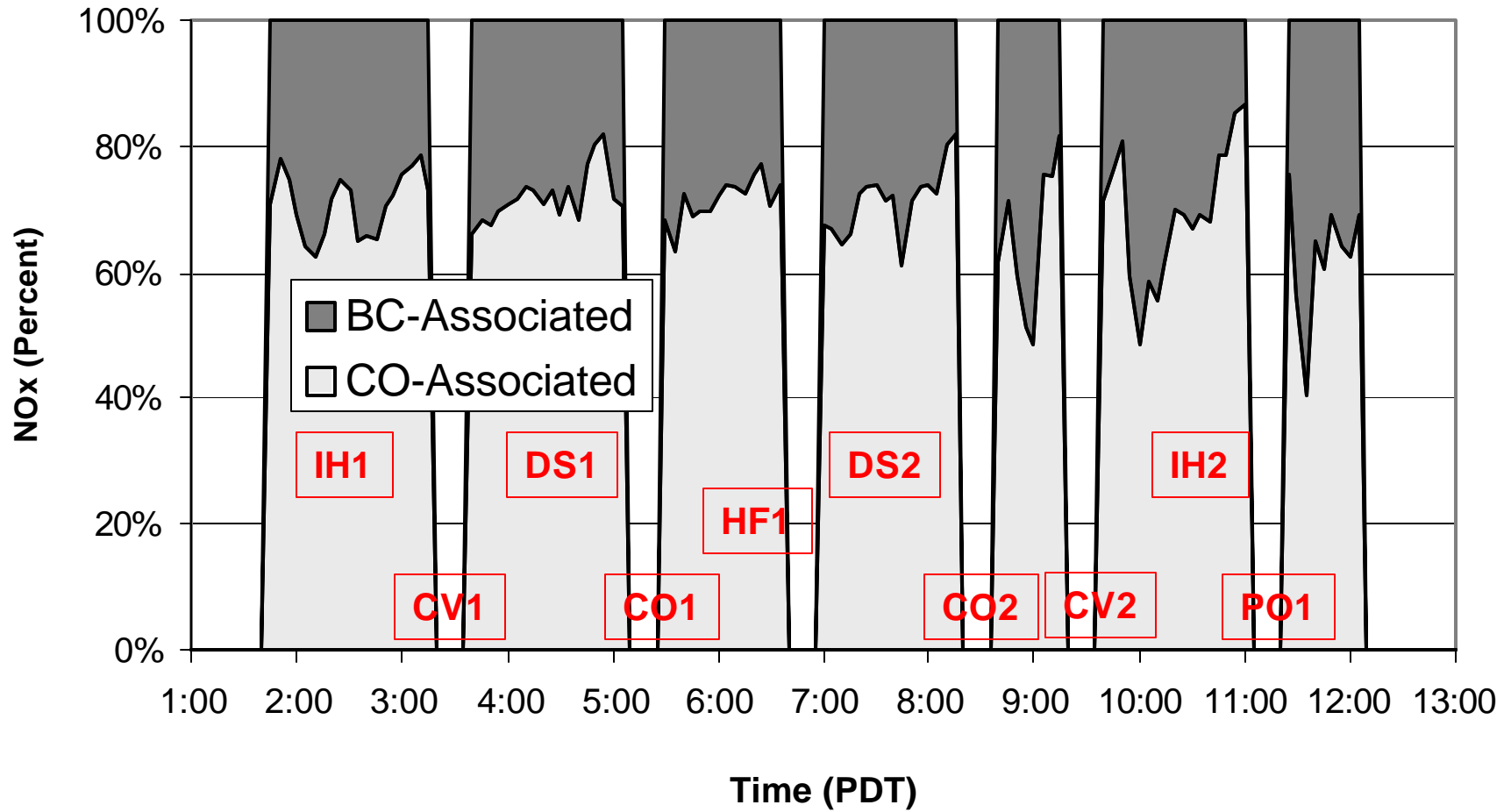
# Azusa



**Ambient NOx Associated with CO and Black Carbon  
Mobile Sampling on 10/4/00 (Wednesday)**



**Ambient NOx Associated with CO and Black Carbon  
Mobile Sampling on 10/8/00 (Sunday)**



# Sampling Locations During the Phase II Field Measurements



## Weekend/Weekday Differences in Ambient NOx Associated with CO and Black Carbon in the SoCAB

Location	Industry Hills		Azusa		Pico Rivera				
Time Interval	10:00 to 10:45		9:00 to noon		9:00 to noon		Mean		
Date	NOx (CO)	NOx (BC)	NOx (CO)	NOx (BC)	NOx (CO)	NOx (BC)	NOx (CO)	NOx (BC)	
Mon, 10/2	37	47	54	56	34	47	42	46 %	50
Wed, 10/4	28	30	26	44	30	33	28	44 %	36
Sat, 10/7	29	18	26	22	25	21	27	57 %	20
Sun, 10/8	31	12	33	19	30	18	31	66 %	16
<u>Ratios</u>									
Sat/Wed	1.01	0.58	1.00	0.50	0.83	0.63	0.94		0.56
Sun/Mon	0.84	0.25	0.61	0.35	0.88	0.39	0.75		0.33

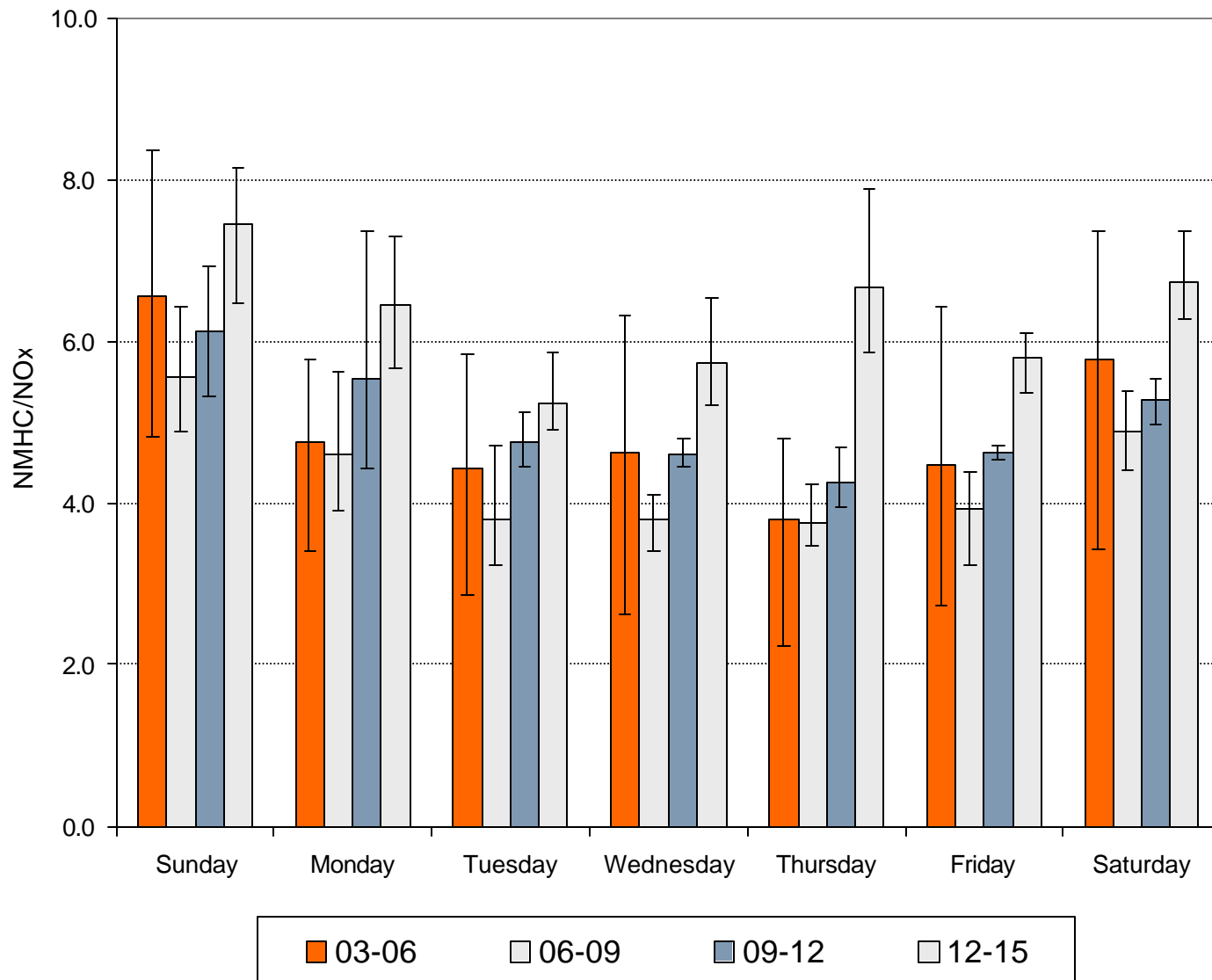
Gasoline vehicles account for 71%  
of total on-road NOx emissions (EMFAC 2000)

## Hypotheses for why ozone is higher on weekends

- **NO<sub>x</sub> timing.** NO<sub>x</sub> emitted later in the morning on weekends into an aged photochemical system causes these emissions to produce ozone more efficiently compared to the NO<sub>x</sub> emitted on weekdays.

## Weekday Variations in NMHC/NO<sub>x</sub> by Period

### Four-Site Means and Standard Deviations of the Means





Mean Wednesday  
 $\pm 1$  sigma

Mean Sunday  
 $\pm 1$  sigma

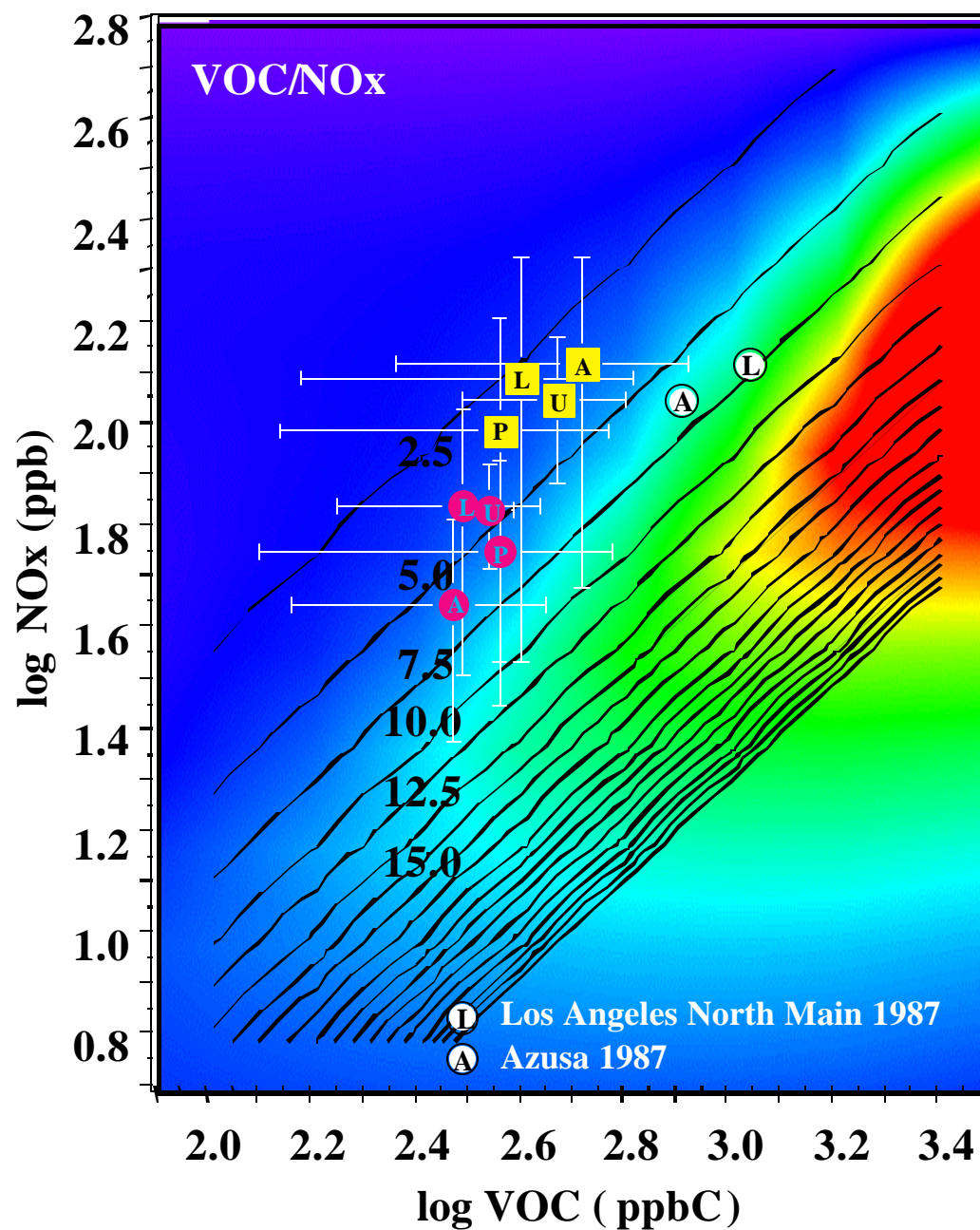
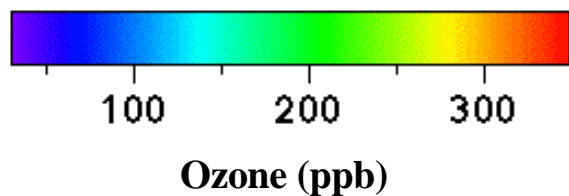
Monitoring Stations

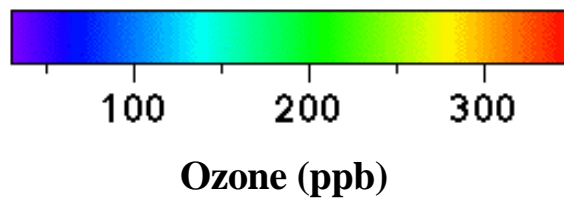
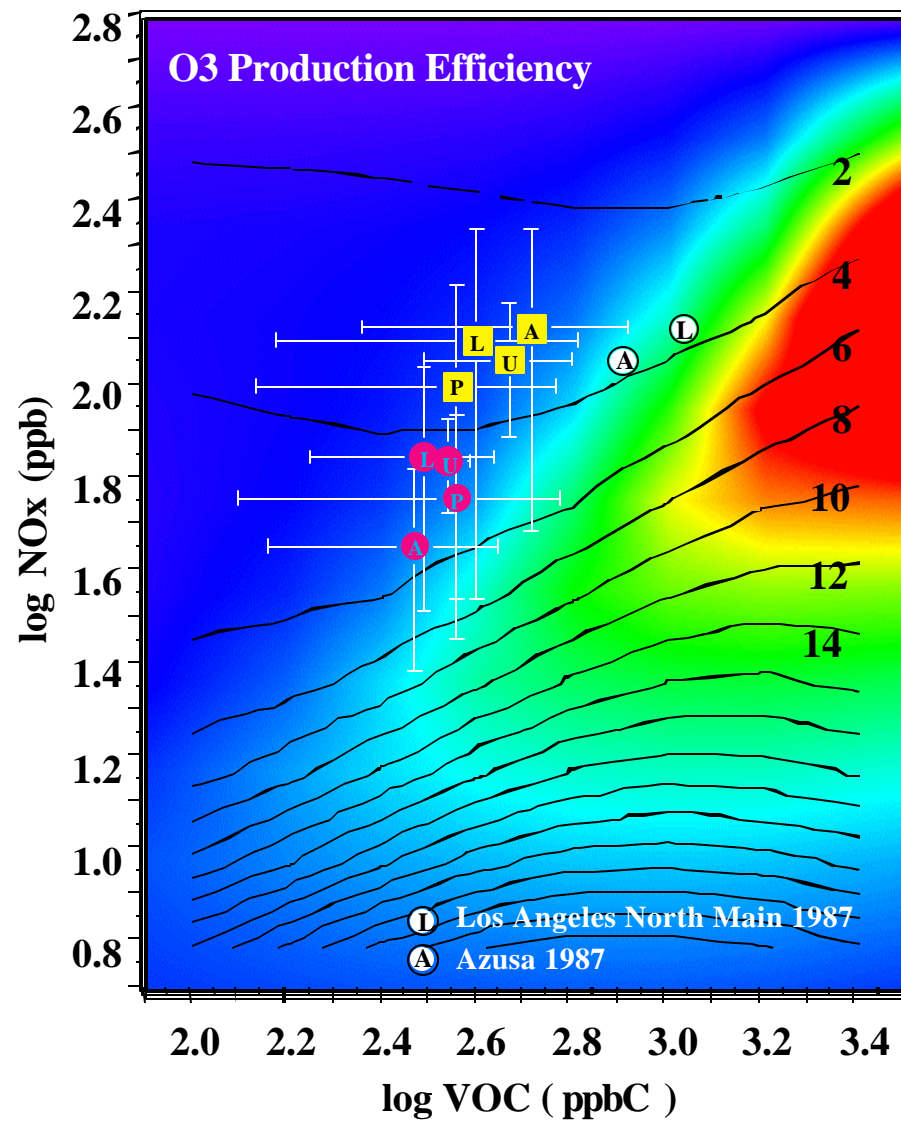
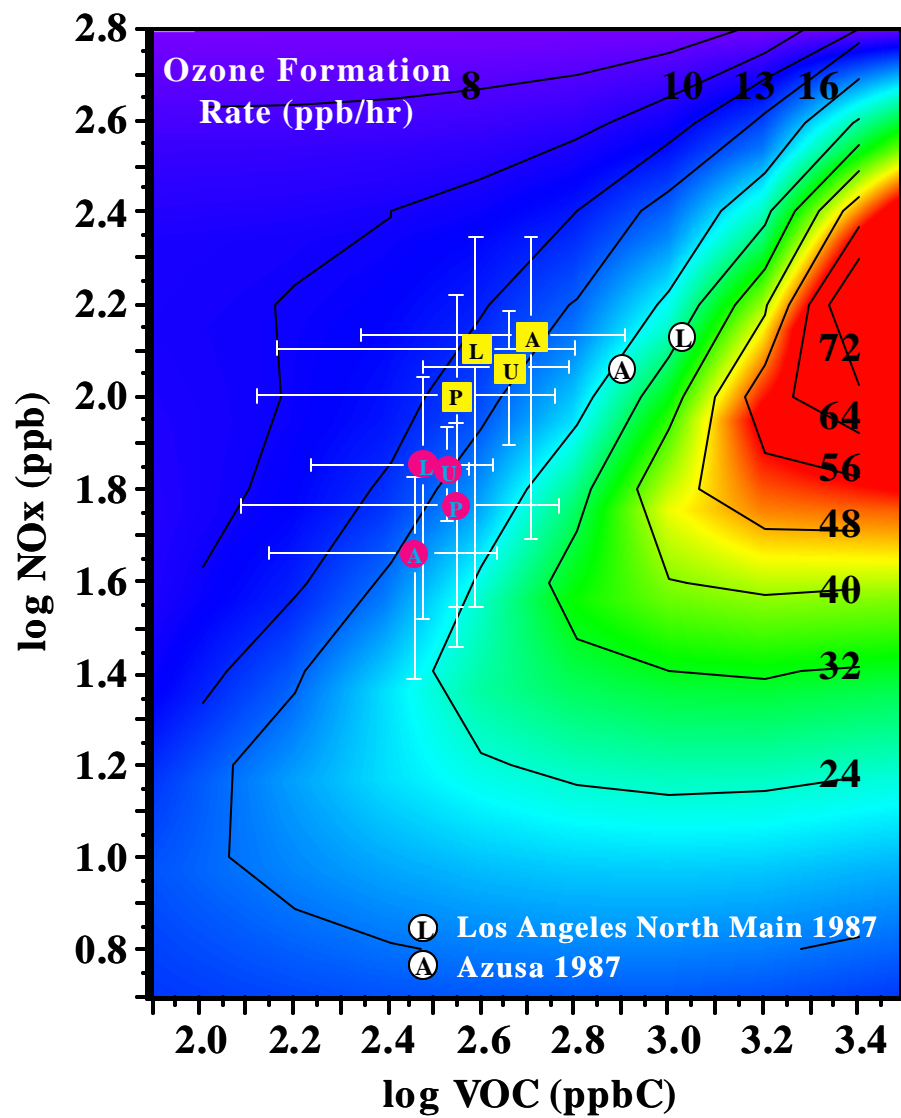
A – Azusa

L – Los Angeles, N. Main

P – Pico Rivera

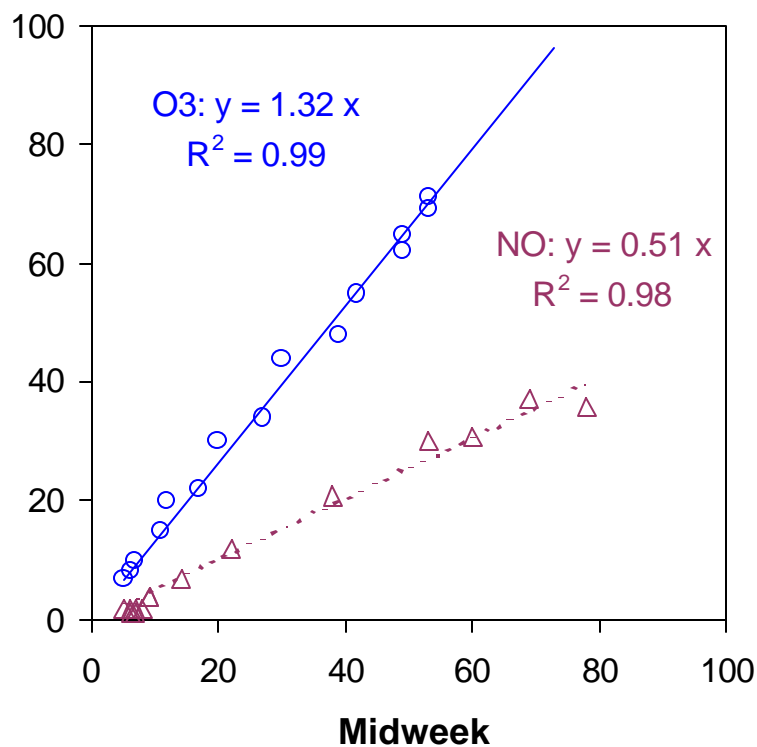
U – Upland



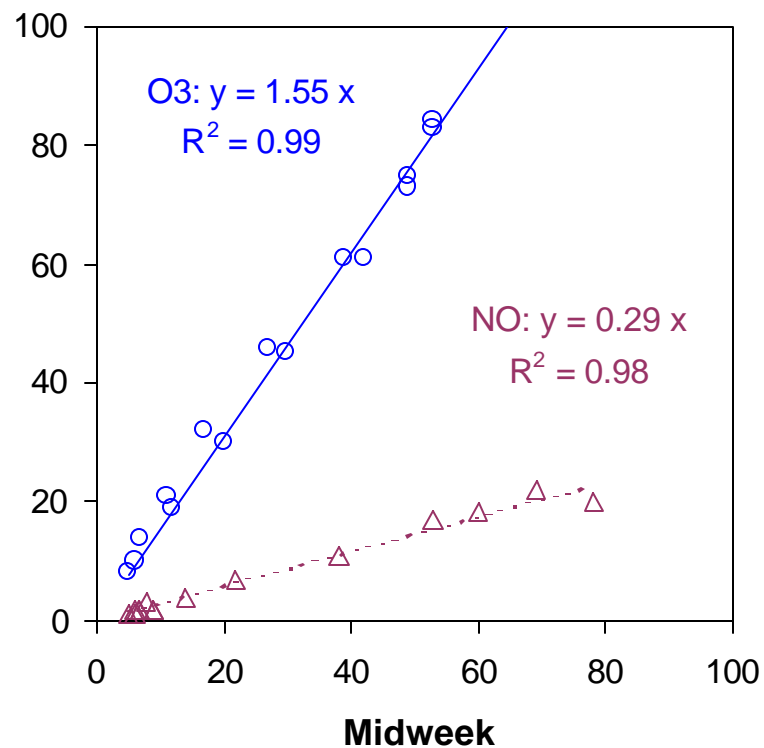


# Correlations of Saturday and Sunday Versus Midweek\* Hourly Daytime (0600 to 2000, PDT) O<sub>3</sub> and NO at Azusa, 1999-2000

**Saturday**



**Sunday**

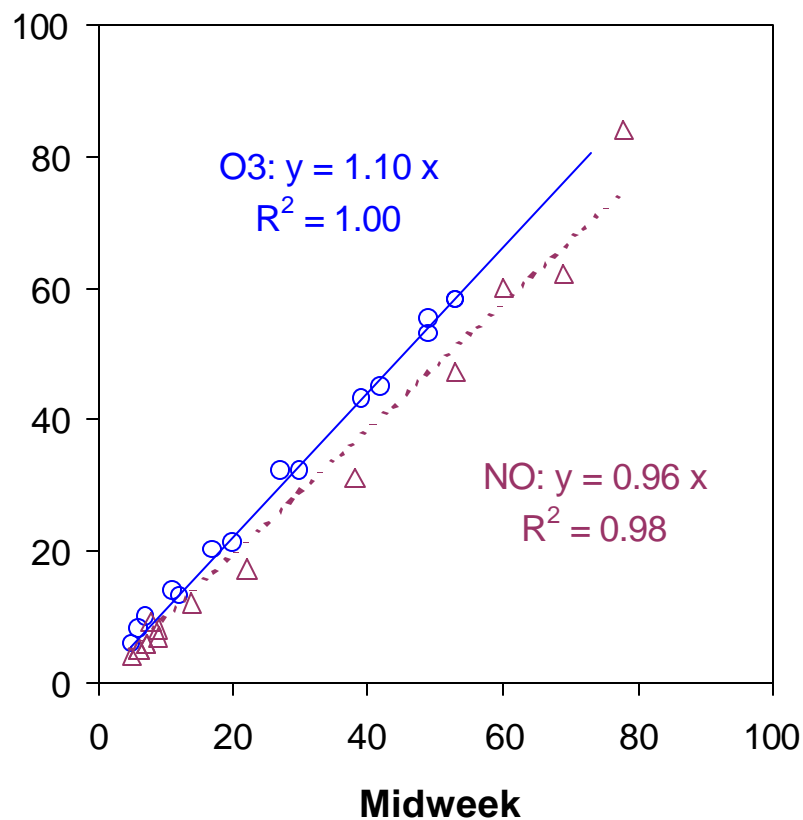


\* Tuesday to Thursday

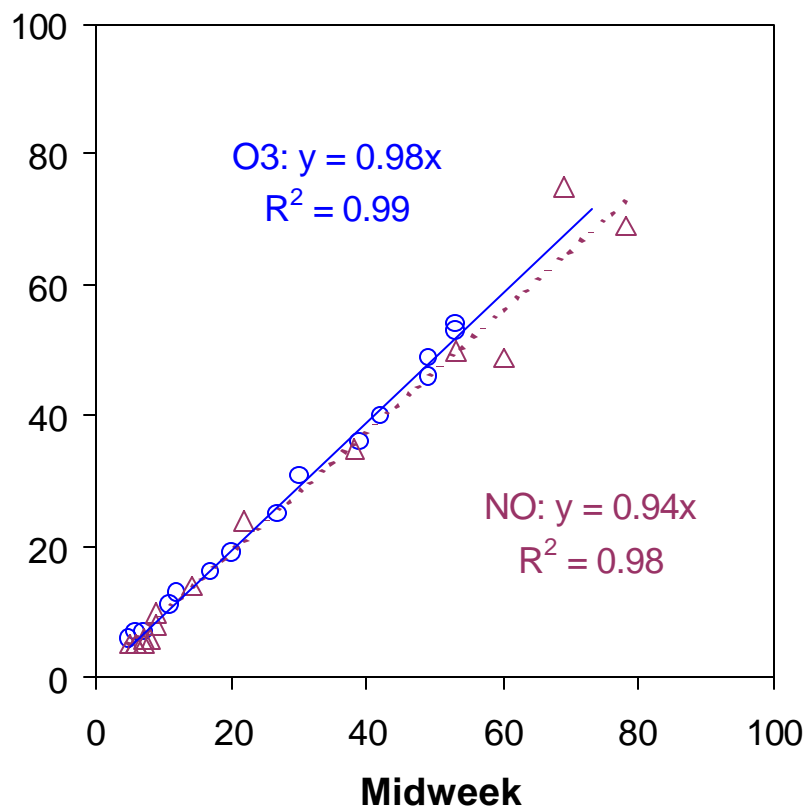
# Correlations of Monday and Friday Versus Midweek\*

## Hourly Daytime (0600 to 2000, PDT) O<sub>3</sub> and NO at Azusa, 1999-2000

Monday



Friday



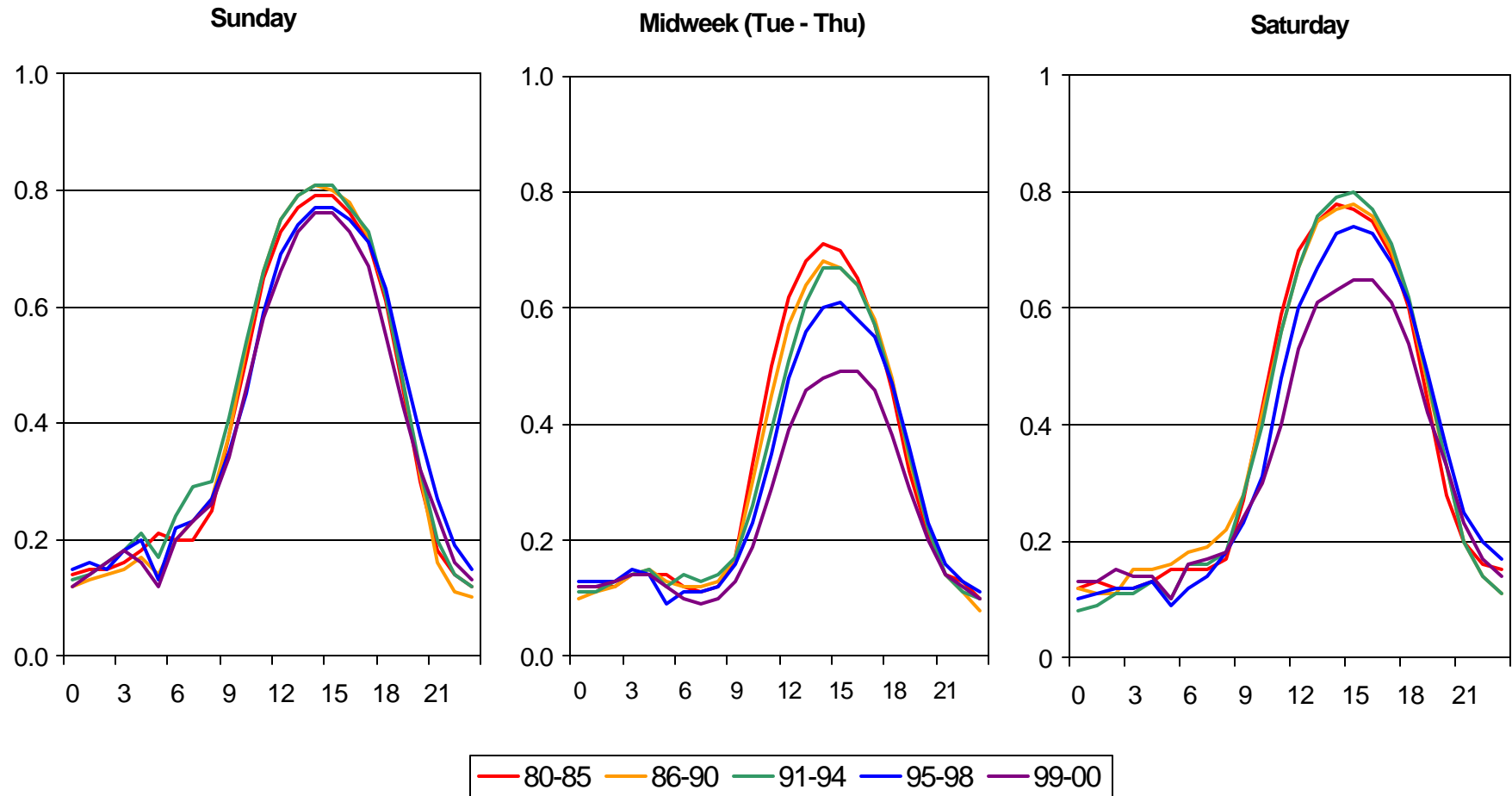
\* Tuesday to Thursday

# Weekday Correlations of Hourly O3 and NO

Location	Daylight (0600-2000)			
	Ozone		Nitric Oxide	
	Slope	R <sup>2</sup>	Slope	R <sup>2</sup>
<u>Friday/Midweek</u> <sup>1</sup>				
Los Angeles N. Main	0.98	1.00	0.89	0.99
Pico Rivera	0.96	1.00	0.86	0.98
Azusa	0.98	0.99	0.94	0.96
Upland	1.02	1.00	1.03	0.99
<u>Saturday/Midweek</u>				
Los Angeles N. Main	1.29	0.98	0.61	0.99
Pico Rivera	1.27	1.00	0.69	0.99
Azusa	1.31	0.99	0.51	0.98
Upland	1.26	0.99	0.62	0.99
<u>Sunday/Midweek</u>				
Los Angeles N. Main	1.49	0.96	0.43	0.97
Pico Rivera	1.50	0.98	0.39	0.99
Azusa	1.55	0.99	0.29	0.98
Upland	1.44	0.97	0.29	0.91
<u>Means</u>				
Friday/Midweek	0.99	1.00	0.93	0.98
Saturday/Midweek	1.28	0.99	0.61	0.99
Sunday/Midweek	1.50	0.98	0.35	0.96

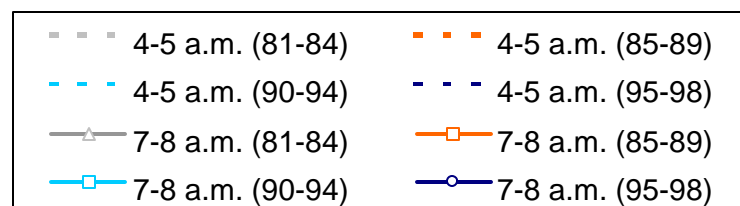
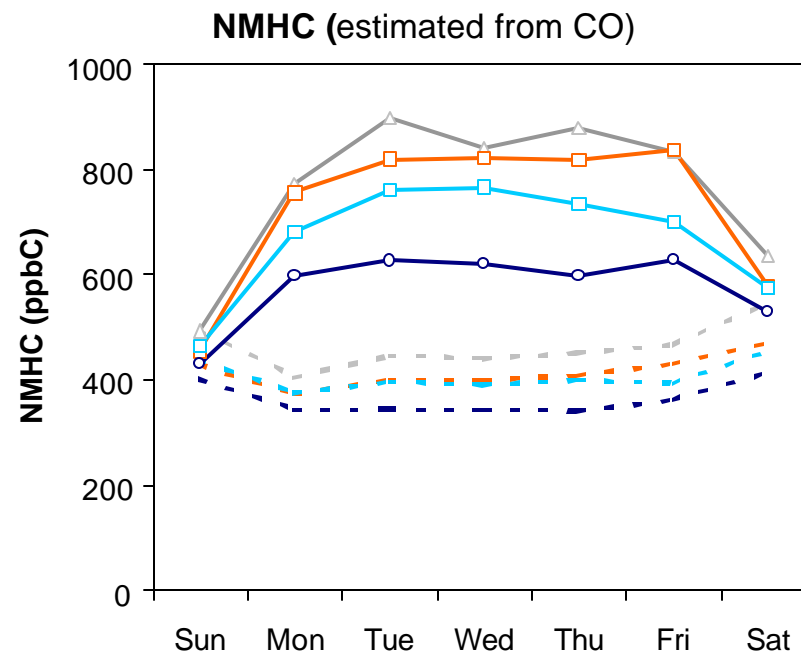
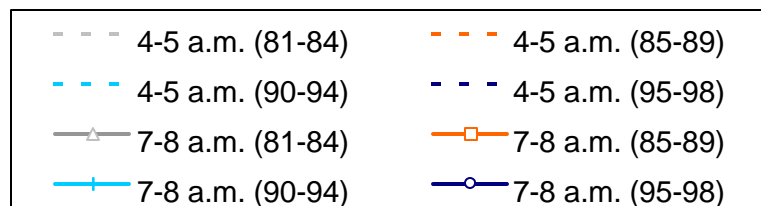
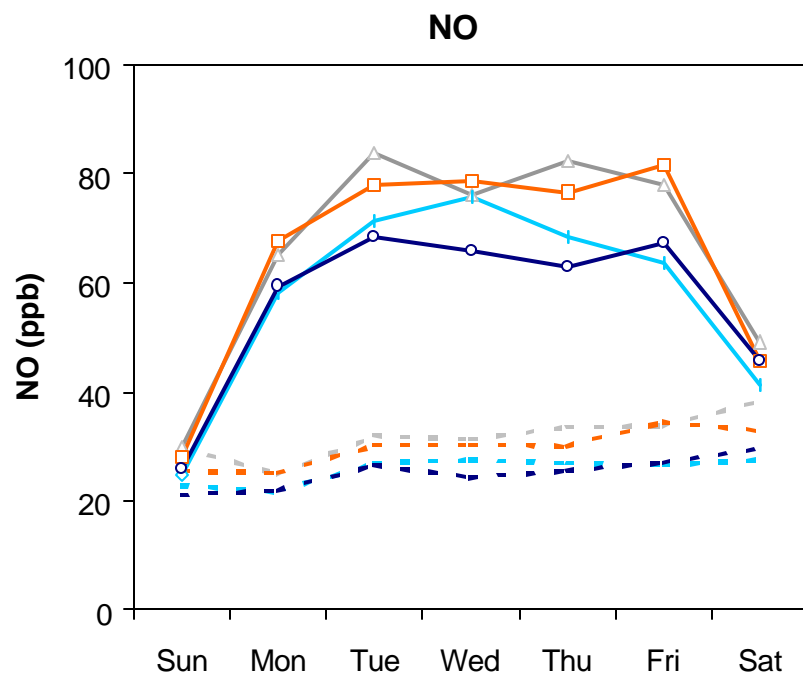
<sup>1</sup> mean to Tuesday, Wednesday, and Thursday

# Ratio of Peak Ozone to Potential Ozone (O<sub>3</sub> + NO<sub>x</sub>) 1980 to 2000



## **Hypotheses for why ozone is higher on weekends**

3. **Pollutant carryover near the ground.** Greater carryover of precursor emissions due to different vehicle activity on Friday and Saturday evening results in increased rate of ozone formation on weekend mornings.



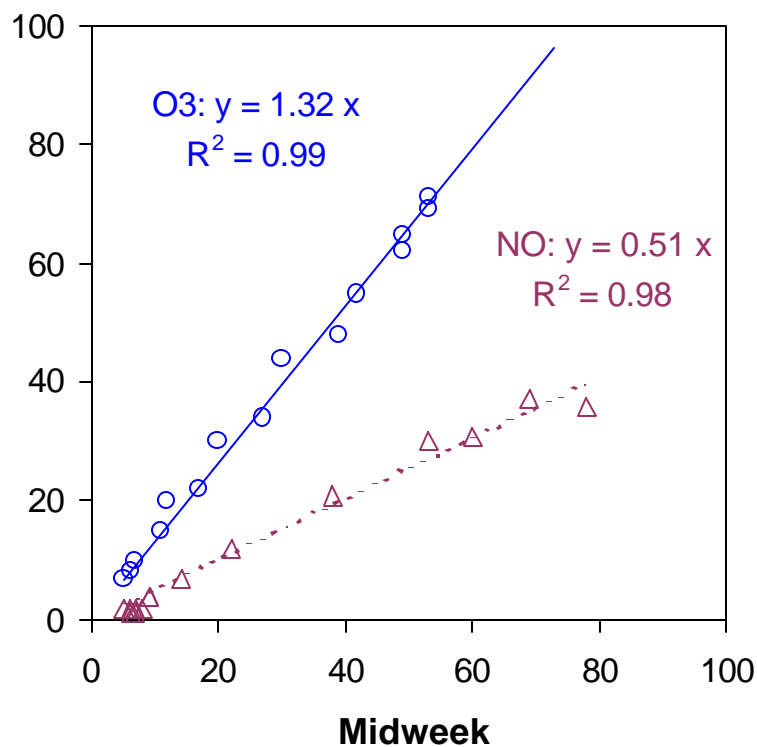


## **Hypotheses for why ozone is higher on weekends**

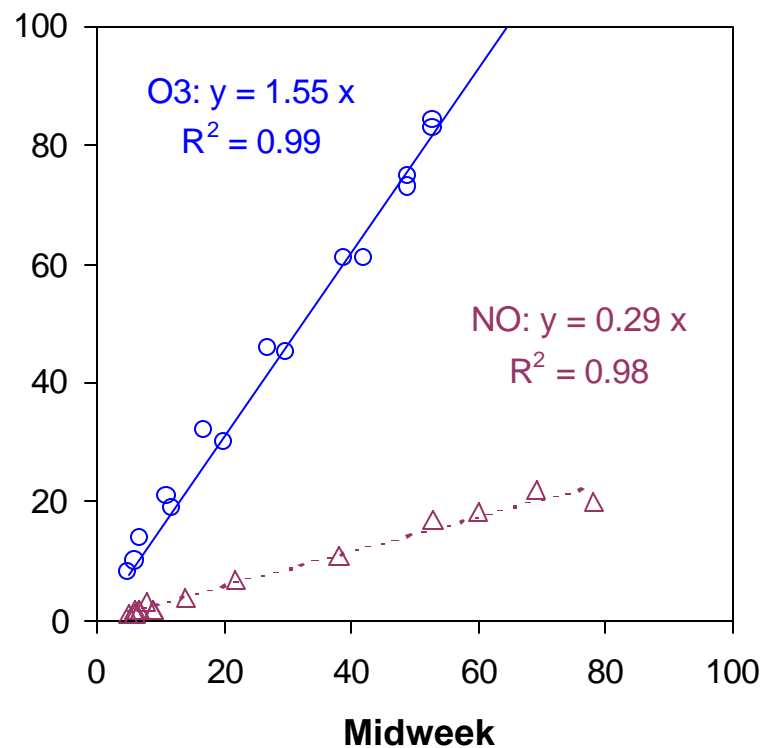
4. **Pollutant carryover aloft.** Carryover of aged pollutants from aloft on weekend has greater influence on weekend mornings due to lower emissions of NO<sub>x</sub>.

# Correlations of Saturday and Sunday Versus Midweek\* Hourly Daytime (0600 to 2000, PDT) O<sub>3</sub> and NO at Azusa, 1999-2000

**Saturday**



**Sunday**

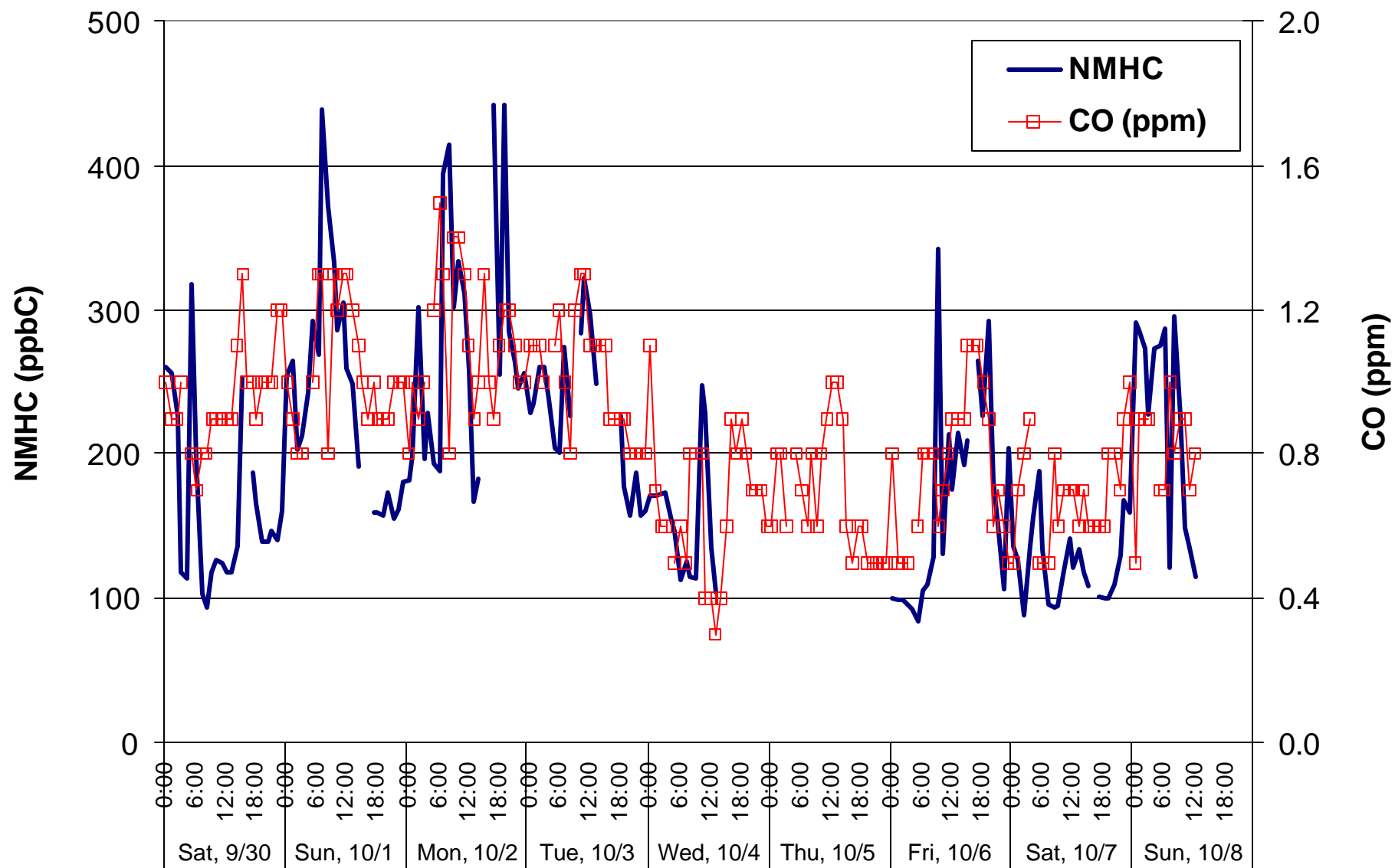


\* Tuesday to Thursday

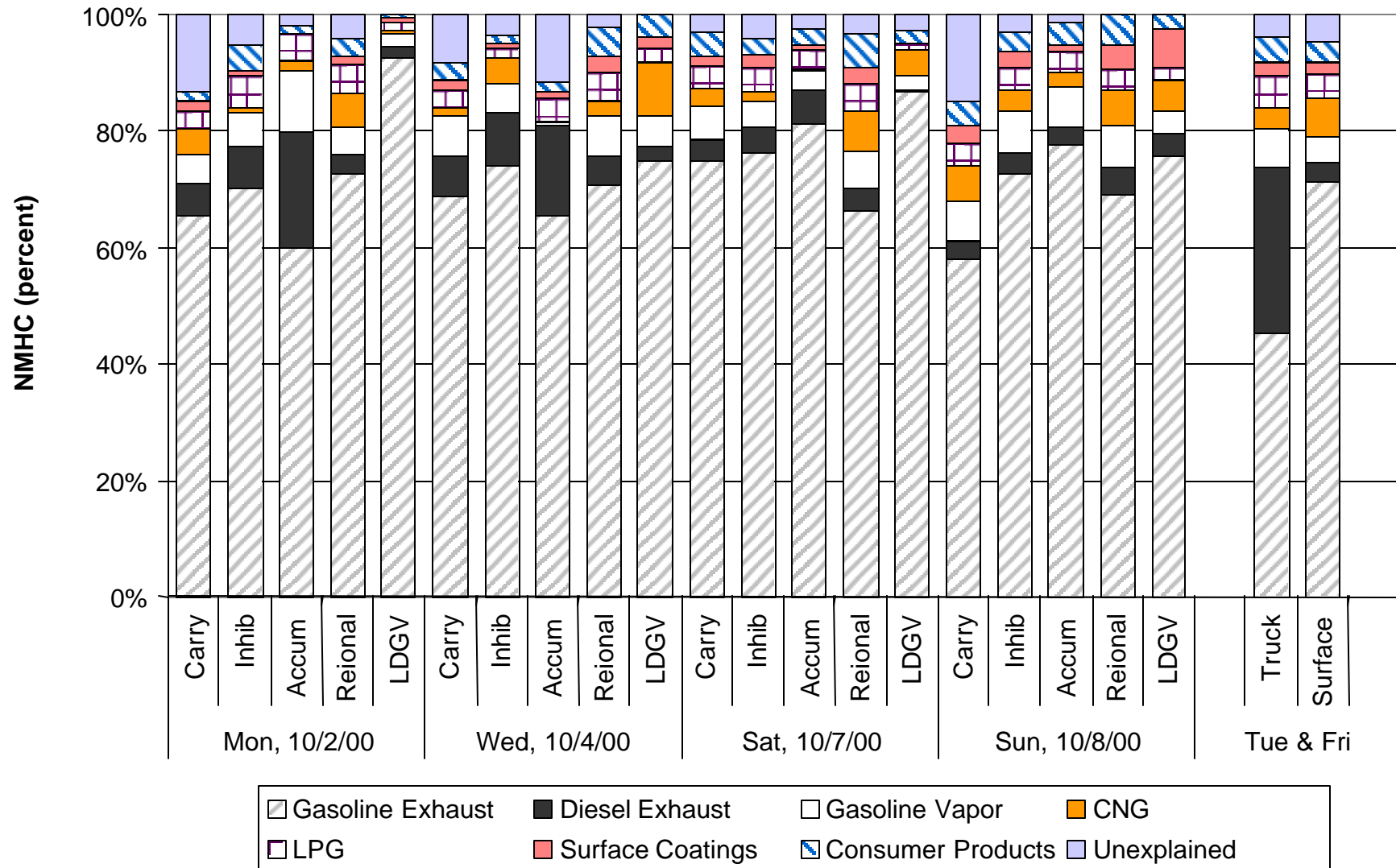
## **Hypotheses for why ozone is higher on weekends**

5. **Increased weekend VOC emissions.** Increased VOC emissions from use of lawn and garden equipment, recreational vehicles, backyard barbecues, and household solvents on weekends results in higher weekend ozone concentrations.

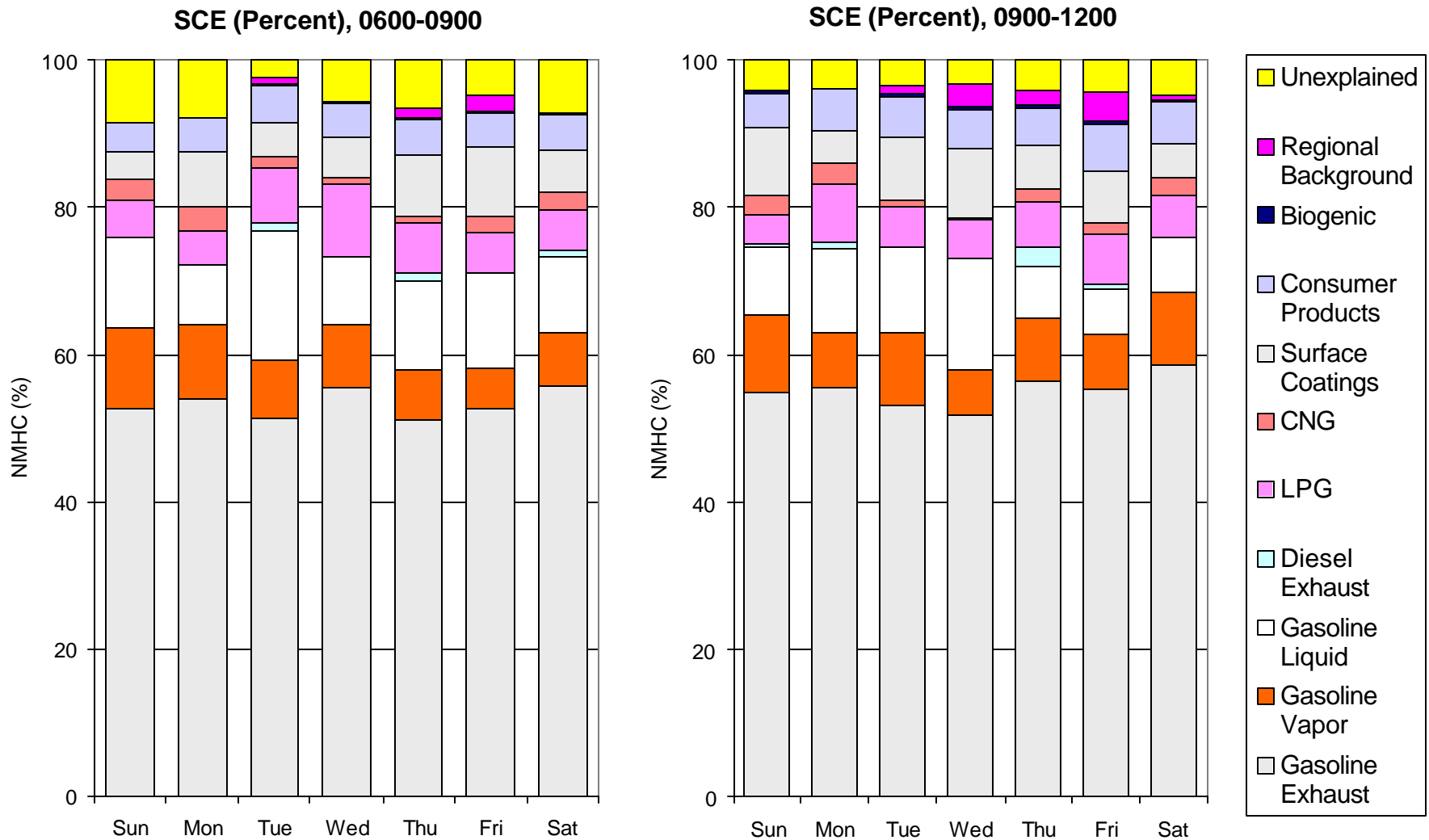
# NMHC and CO at Azusa, 9/30/00 to 10/8/00



# Source Apportionment of NMHC During Phase II Field Study



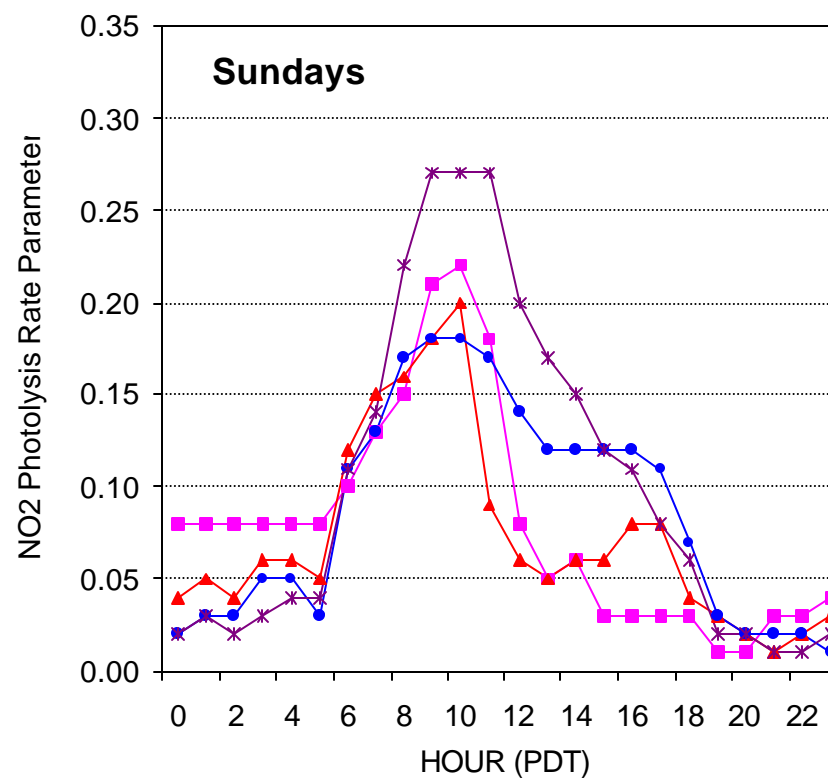
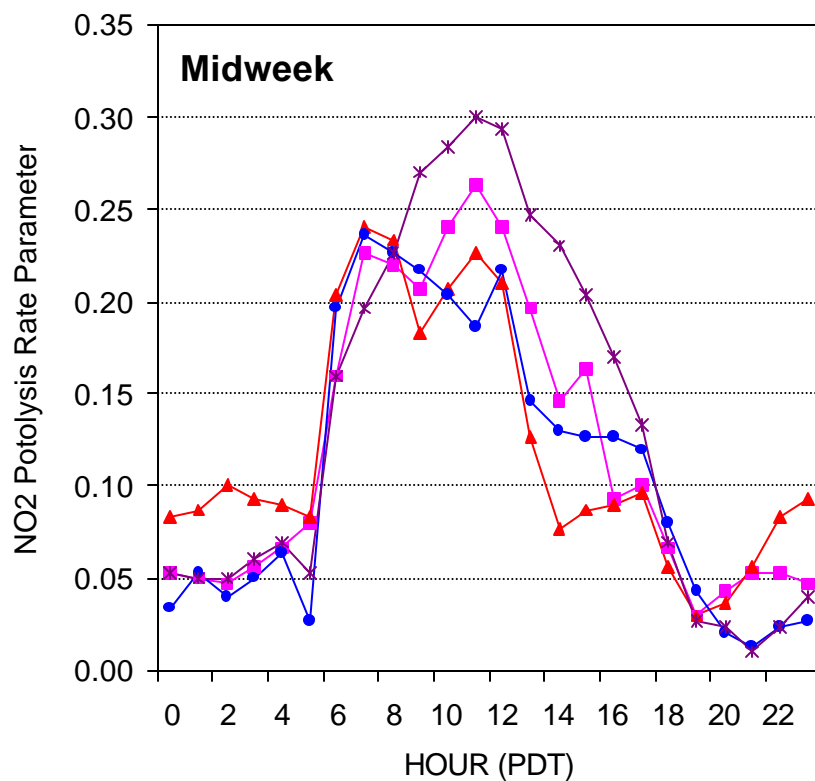
# Mean Weekday Variations in Source Apportionment of NMHC At Azusa, Summer 2000



## **Hypotheses for why ozone is higher on weekends**

- 6. Increased photolysis due to decreased emissions of fine particles.** Lower PM concentrations during weekends increase radiation available for photolysis, thus increasing the rate of ozone formation compared to weekdays.

## Estimated Photolysis Rate Parameter ( $J_{\text{NO}_2}$ ) at Azusa



80-85

86-90

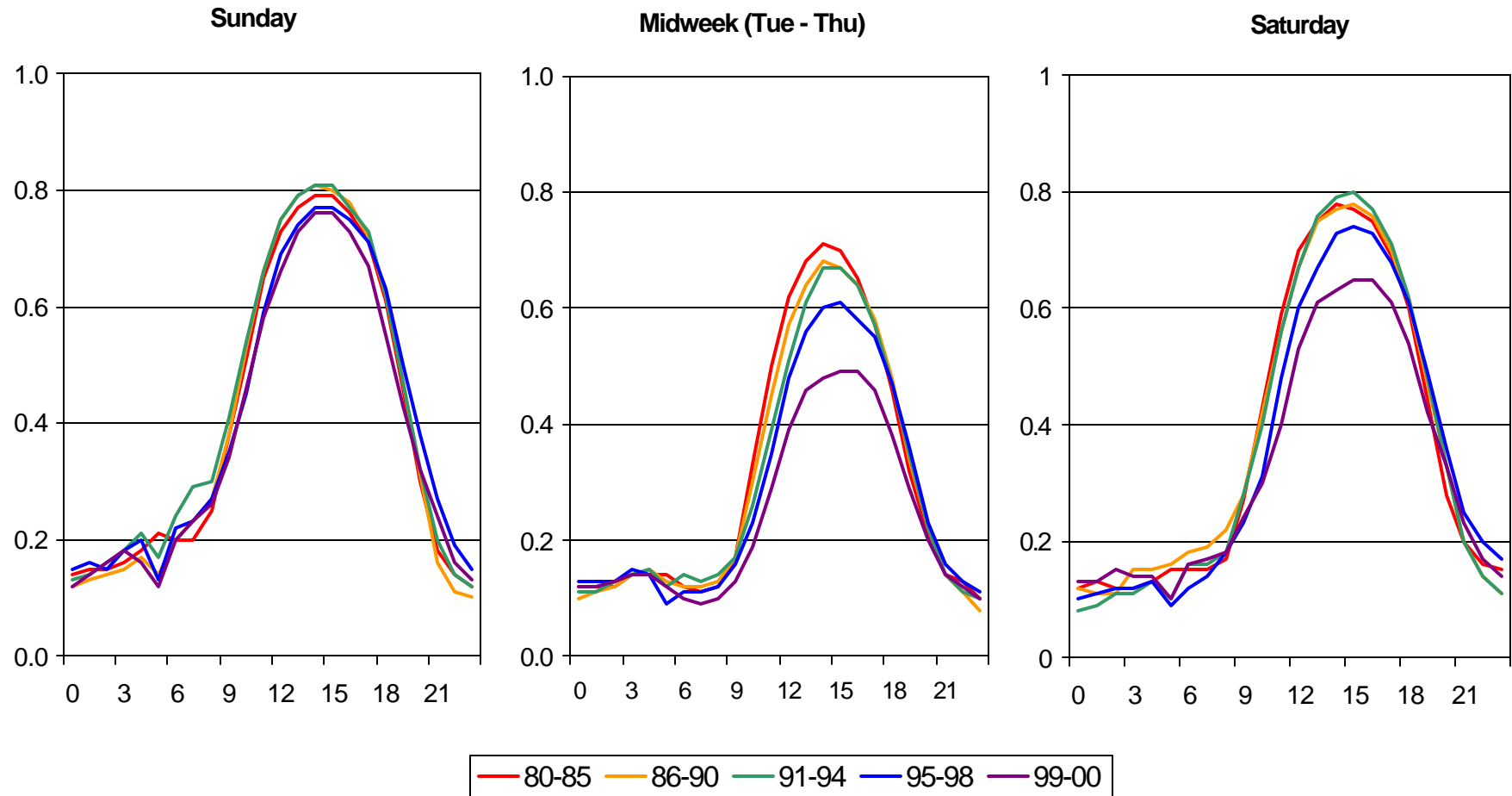
91-94

95-98

99-00



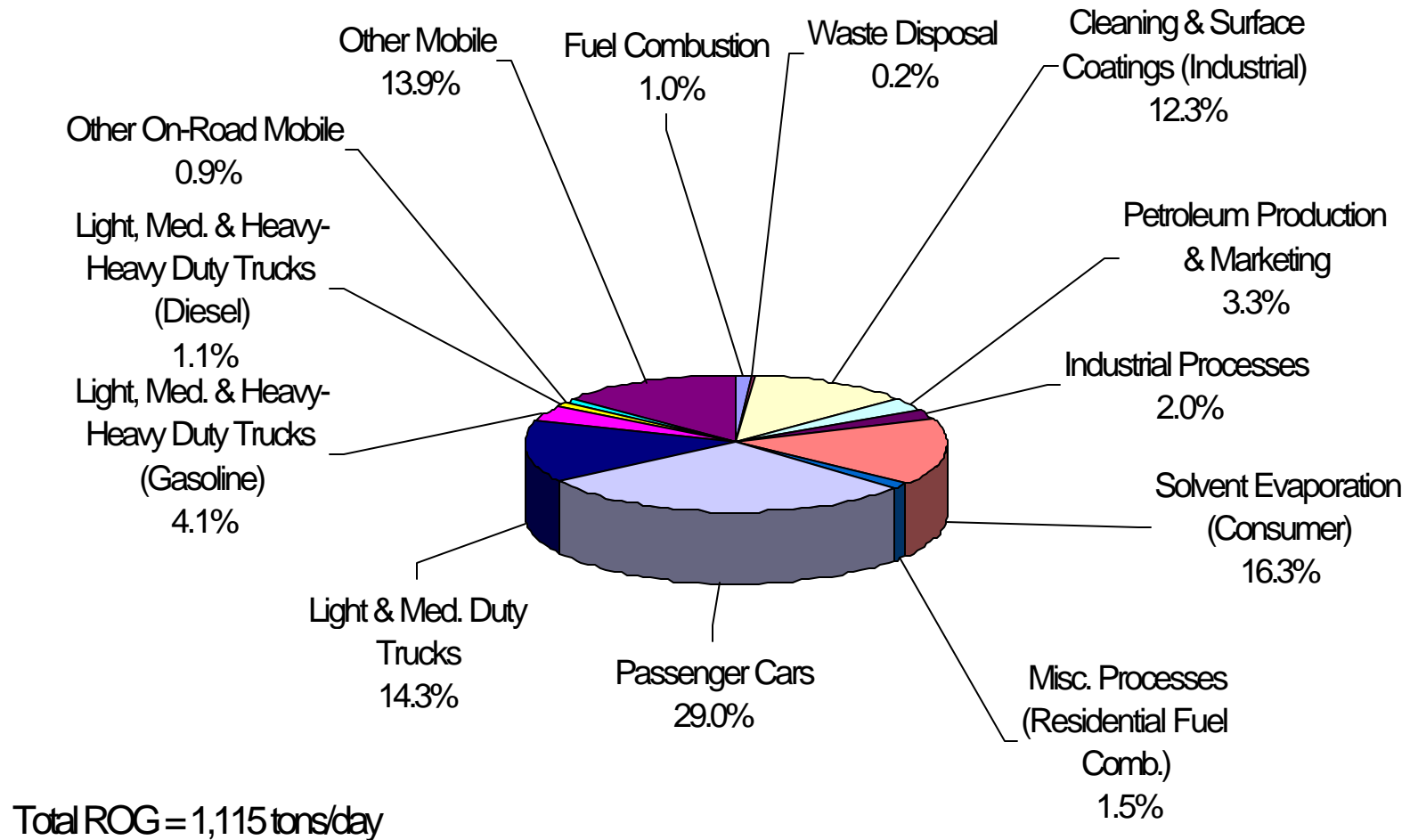
# Ratio of Peak Ozone to Potential Ozone (O<sub>3</sub> + NO<sub>x</sub>) 1980 to 2000



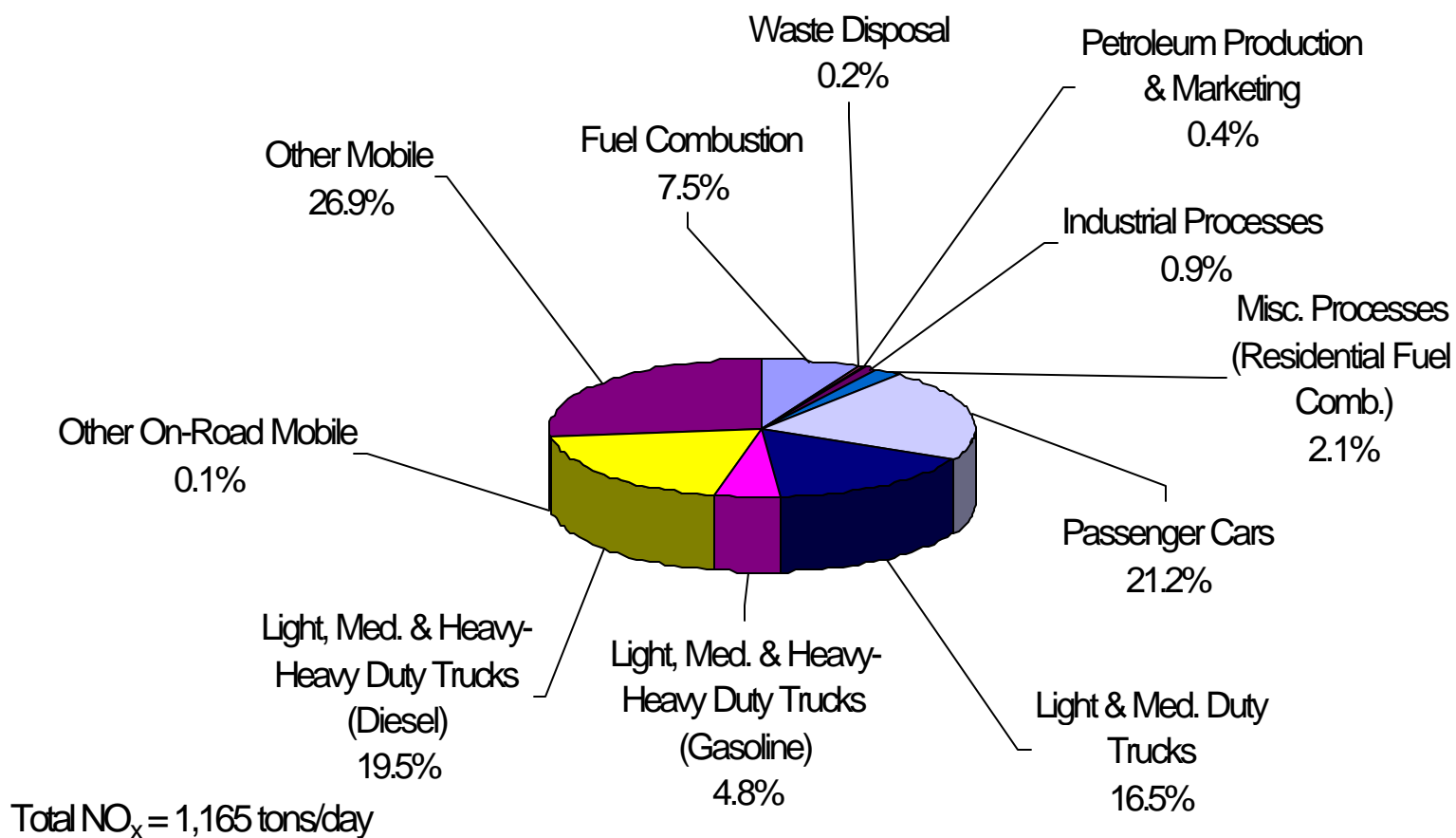
# **SUMMARY OF FINDINGS**

**Sonoma Technology, Inc.**

# SoCAB ROG Emission Inventory



# SoCAB NO<sub>x</sub> Emission Inventory



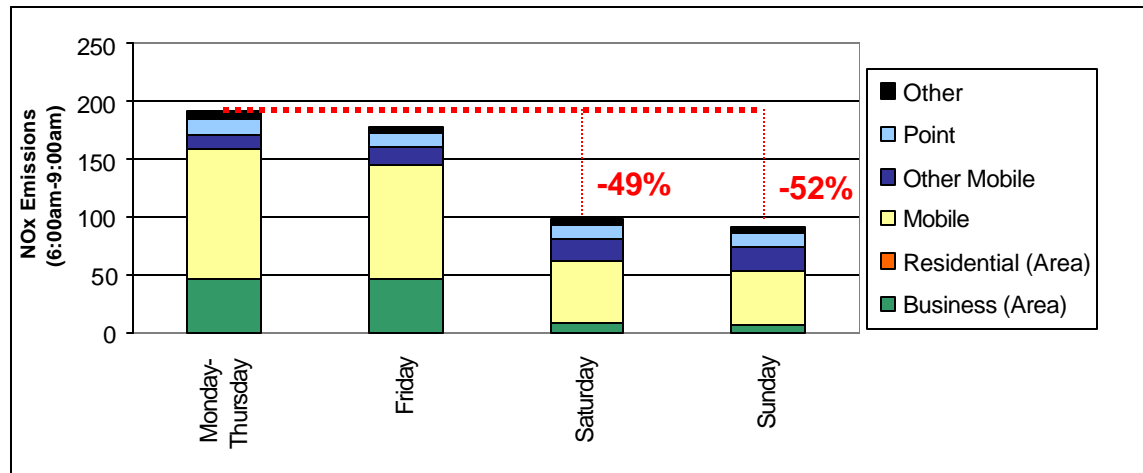
## Hypothesis 1 – NO<sub>x</sub> Reduction (1 of 3)

- **NO<sub>x</sub> reduction**

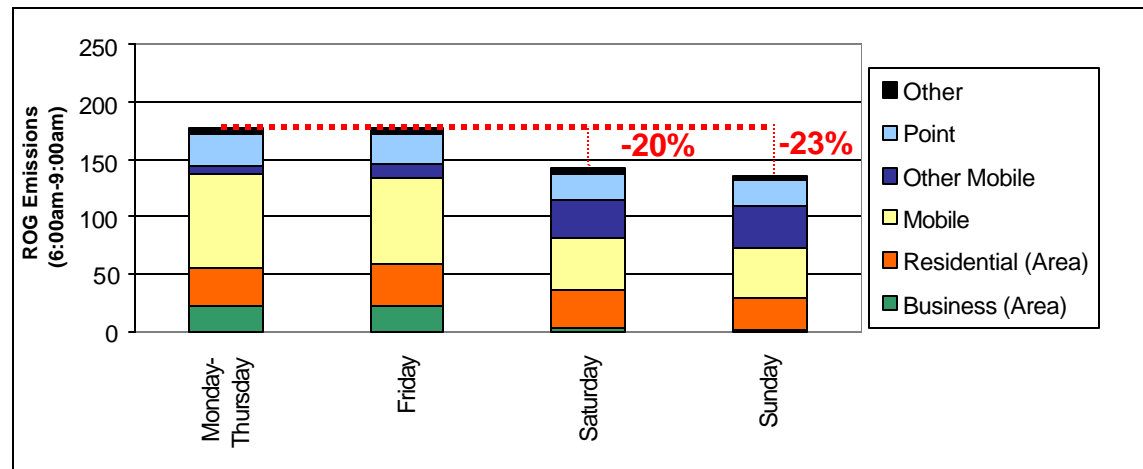
Lower concentrations of NO<sub>x</sub> on weekend mornings lead to higher ozone concentrations on weekends because the accumulation of ozone begins earlier on weekends due to less titration of ozone with NO and because of the higher rate of ozone accumulation due to higher VOC/NO<sub>x</sub> ratios.

# Hypothesis 1 – NO<sub>x</sub> Reduction (2 of 3)

Average 6:00am – 9:00am Emissions - 2000

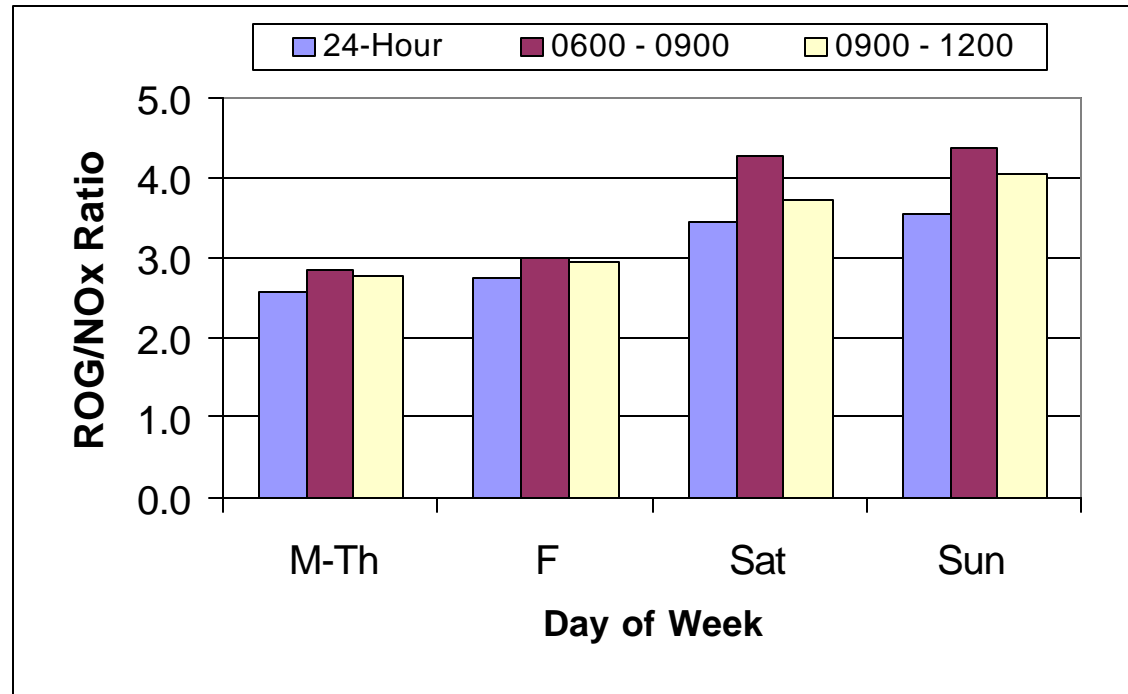


- NO<sub>x</sub> decreases 49% from weekdays to Saturday; 52% Sunday



- ROG decreases 20% from weekdays to Saturday; 23% Sunday
- Relatively larger decreases in NO<sub>x</sub>

## Hypothesis 1 – NO<sub>x</sub> Reduction (3 of 3)



- Higher ROG/NO<sub>x</sub> ratios are generally more favorable for ozone production.
- Molar ratio of ROG/NO<sub>x</sub> is higher on Saturday and Sunday.
- ROG/NO<sub>x</sub> ratio increase is enhanced during ozone forming hours (6:00am – 12:00pm).

## Hypothesis 2 – NO<sub>x</sub> Timing (1 of 3)

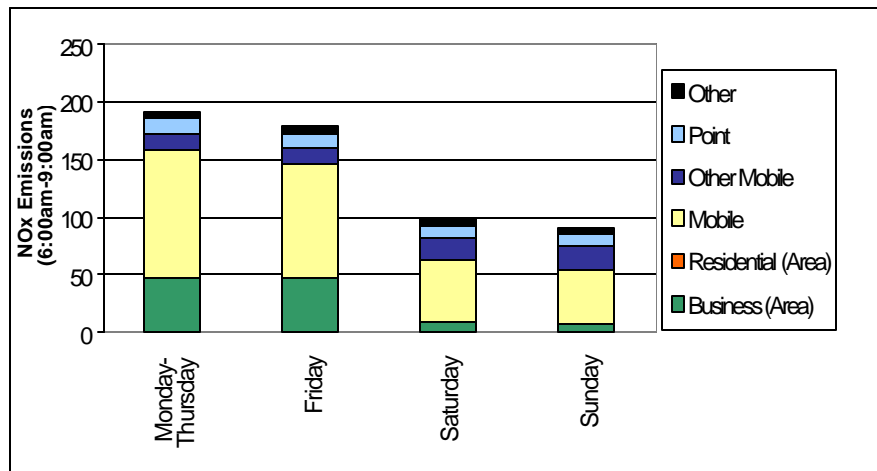
- **NO<sub>x</sub> timing**

NO<sub>x</sub> emitted later in the morning on weekends into an aged photochemical system causes these emissions to produce ozone more efficiently compared to the NO<sub>x</sub> emitted on weekdays.

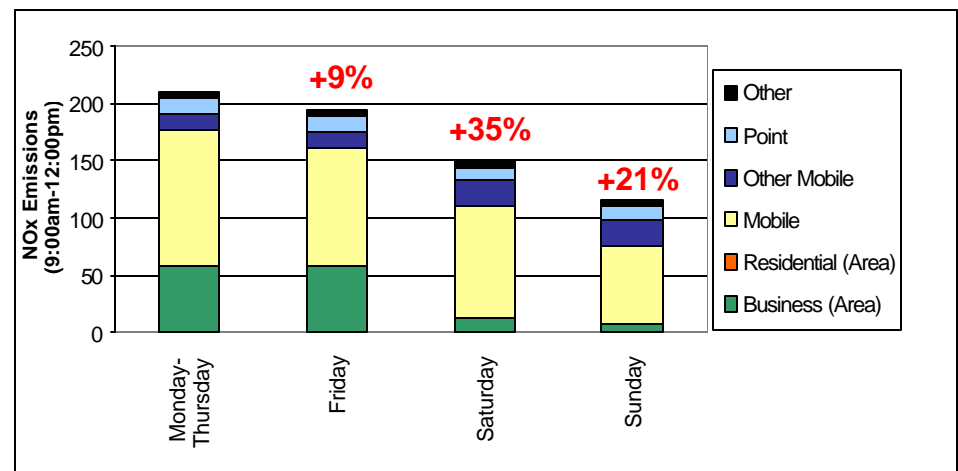


## Hypothesis 2 – NO<sub>x</sub> Timing (2 of 3)

Average 6:00 a.m. – 9:00 a.m. NO<sub>x</sub> Emissions



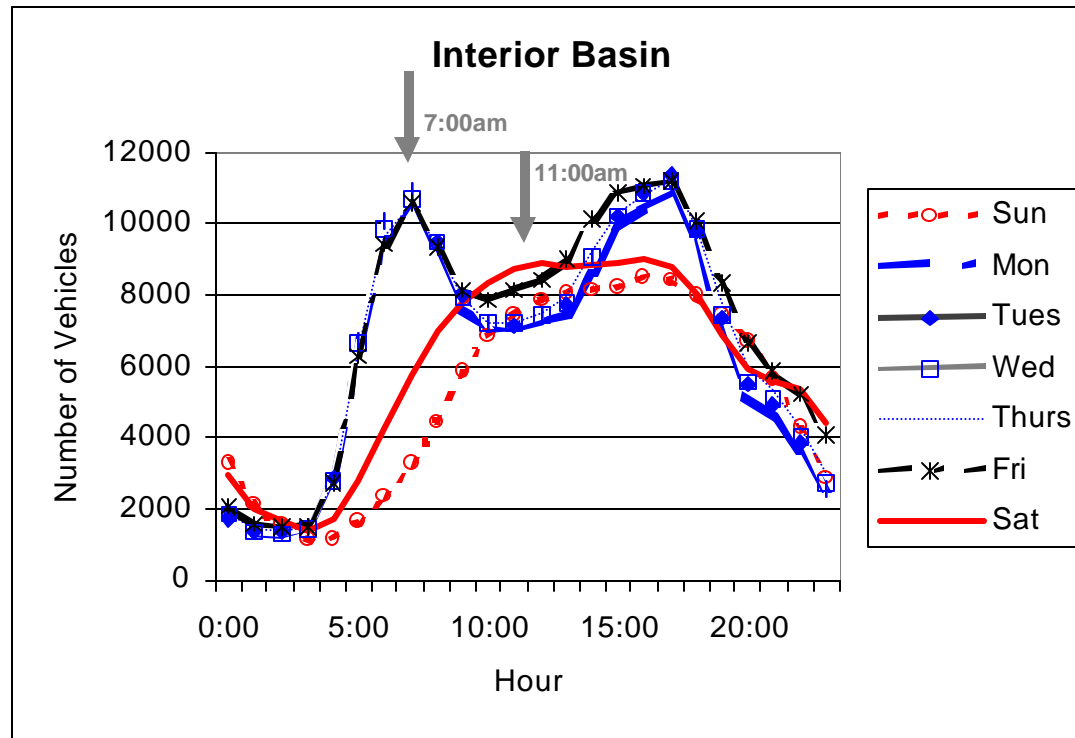
Average 9:00 a.m. – 12:00 p.m. NO<sub>x</sub> Emissions



- Relative increase in NO<sub>x</sub> emissions from 6:00 a.m. – 12:00 p.m. is greater on Saturday and Sunday than on weekdays.

## Hypothesis 2 – NO<sub>x</sub> Timing (3 of 3)

Light Duty Vehicle Traffic Volume by Day of Week



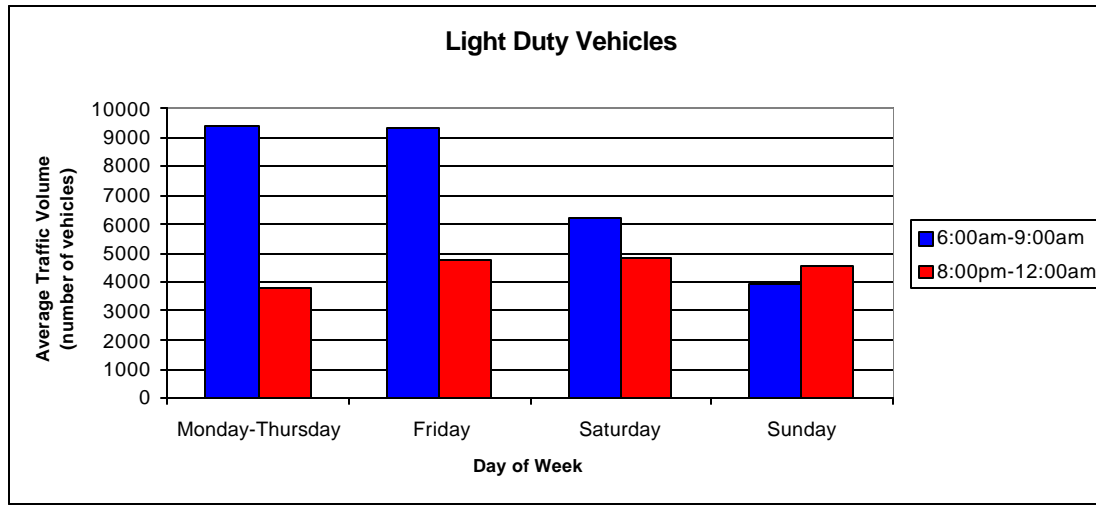
- Morning peak of motor vehicle activity is delayed on weekends.

## Hypothesis 3 – Ground-level carryover (1 of 3)

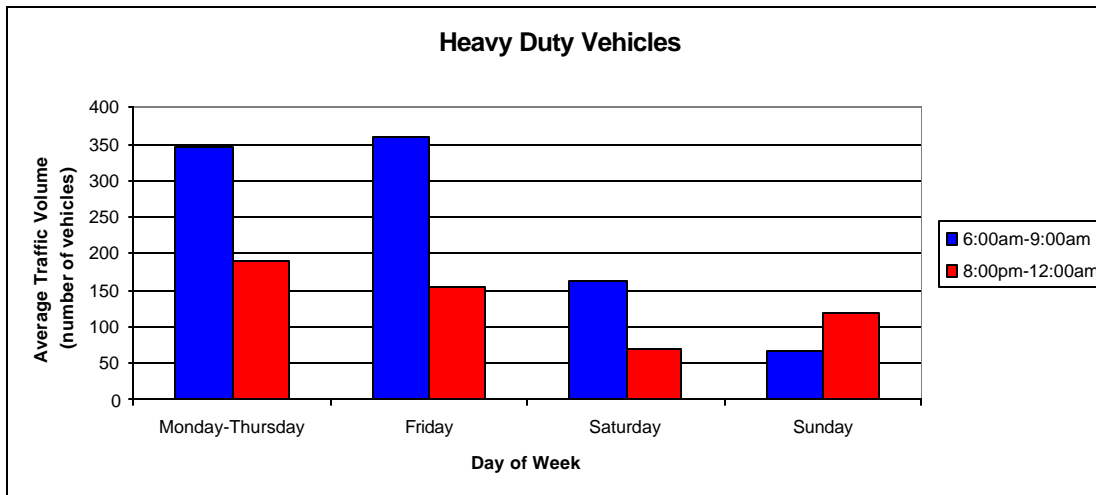
- **Pollutant carryover near the ground**

Greater carryover of precursor emissions due to different vehicle activity on Friday and Saturday evening results in increased rate of ozone formation on weekend mornings.

## Hypothesis 3 – Ground-level carryover (2 of 3)



- Friday, Saturday, and Sunday 8:00 p.m. – 12:00 a.m. traffic volumes for LDV are *higher* than weekdays.



- Friday, Saturday, and Sunday 8:00 p.m. – 12:00 a.m. traffic volumes for HDV are *lower* than weekdays.

## Hypothesis 3 – Ground-level carryover (3 of 3)

- Weekend nights ~1000 *more* light duty vehicles than weekdays (about 25%)
- Weekend nights ~ 50 *fewer* heavy duty vehicles than weekdays (about 20 – 80%)
- NO<sub>x</sub> emission factor from HDV approximately 23 times higher than LDV (more than offsetting LDV)

## Hypothesis 4 – Pollutant carryover aloft (1 of 1)

- Pollutant concentrations aloft are significantly lower than in the past.
- For example on episode mornings:
  - 1987 Ozone aloft = 100-200 ppb
  - 1997 Ozone aloft = 60-100 ppb

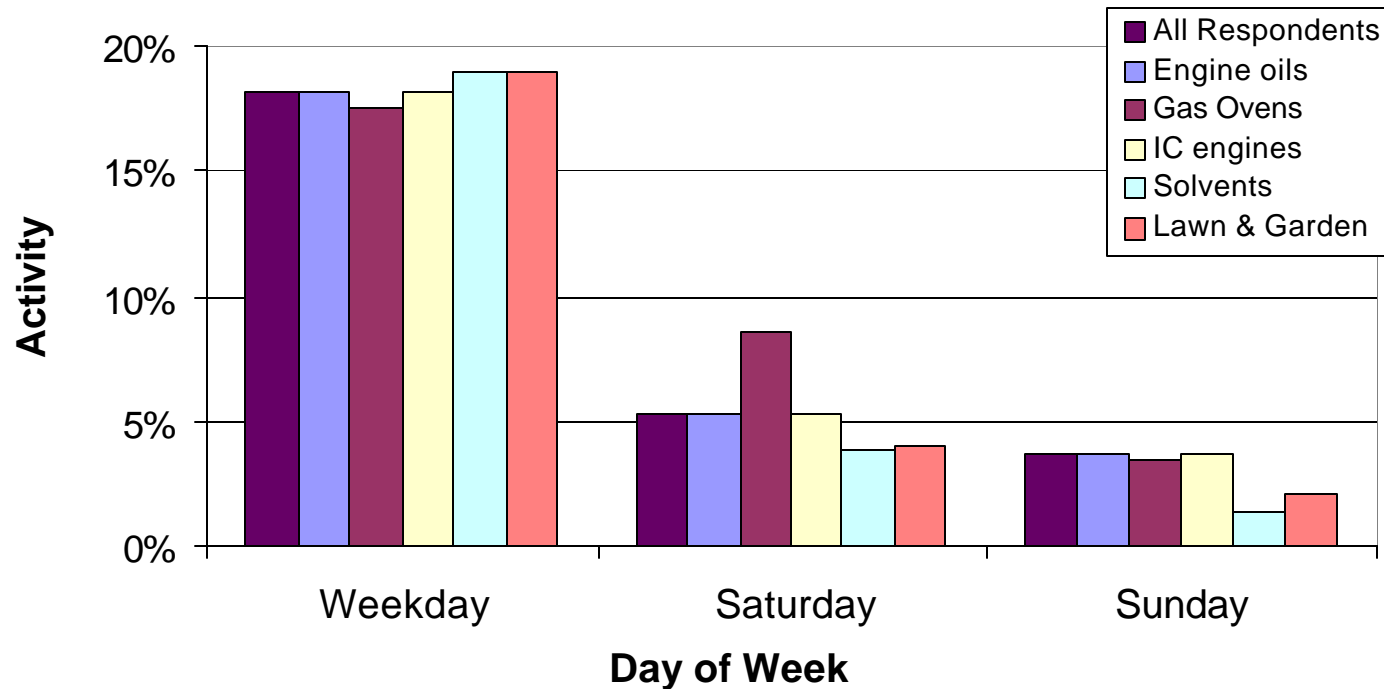
## Hypothesis 5 – Increased weekend VOC (1 of 4)

- **Increased weekend VOC emissions**

Increased VOC emissions from use of lawn and garden equipment, recreational vehicles, backyard barbecues, and household solvents on weekends results in higher weekend ozone concentrations.

## Hypothesis 5 – Increased weekend VOC (2 of 4)

### Business Activity

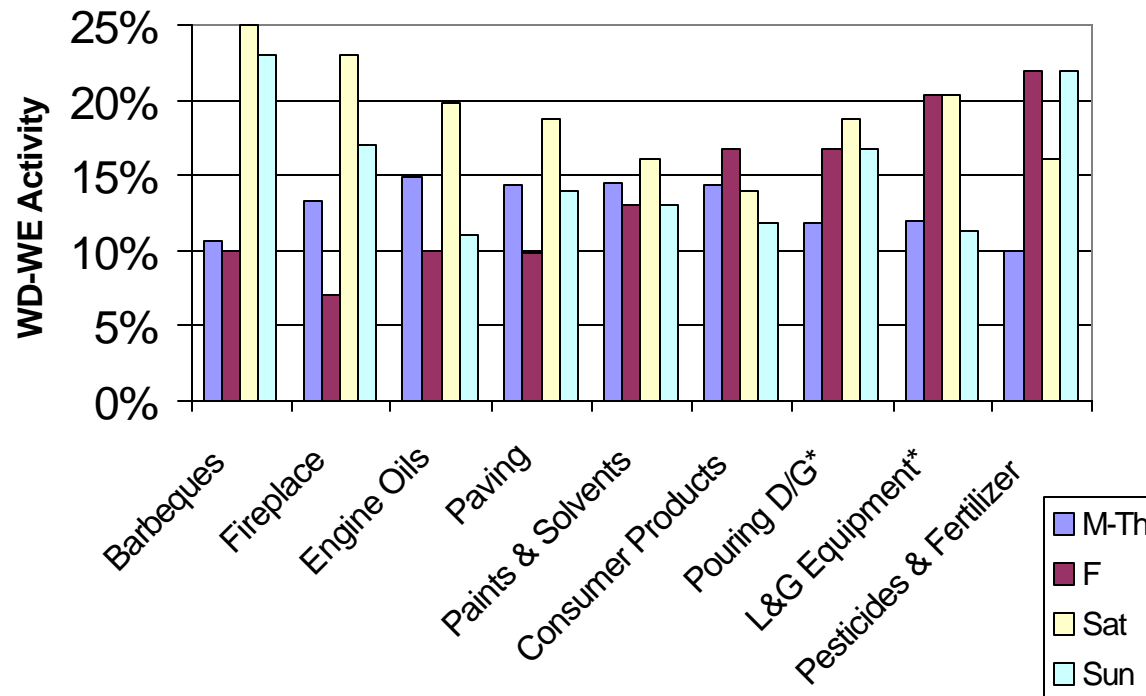


- Emissions activity is much lower on weekends than weekdays for small business.



## Hypothesis 5 – Increased weekend VOC (3 of 4)

### Residential Activity

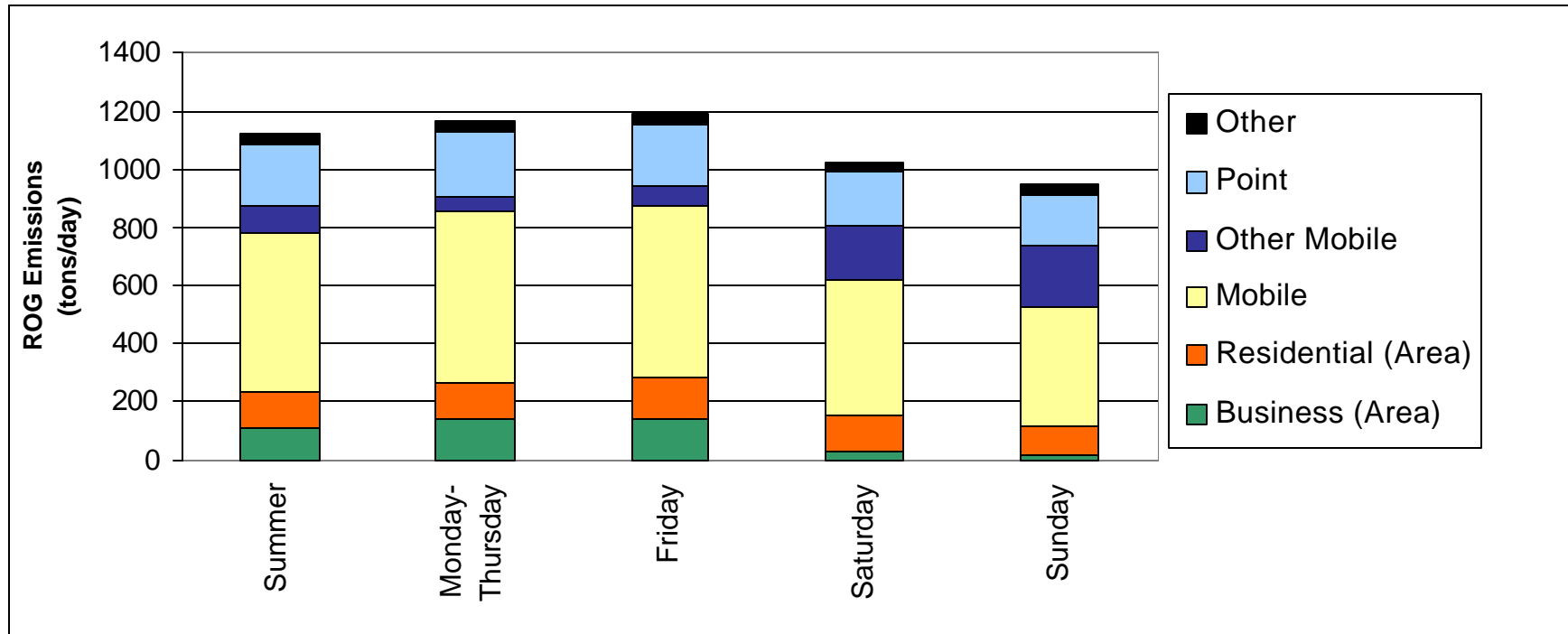


- Emissions activity is higher on weekends than weekdays for residences.

- Recreational boats account for approximately six times as much emissions on weekends compared to weekdays.

## Hypothesis 5 – Increased weekend VOC (4 of 4)

### 2000 Daily Emissions



- Overall ROG emissions are reduced.

**CONCLUSIONS**

**AND**

**RECOMMENDATIONS**

- **NO<sub>x</sub> reduction.** Lower NO<sub>x</sub> on weekend mornings leads to higher ozone on weekends because the accumulation of ozone begins earlier on weekends due to less titration of ozone with NO and because of the higher rate of ozone accumulation due to higher VOC/NO<sub>x</sub> ratios.
- Total emissions in the SoCAB from all categories (including off-road categories) in summer 2000 are about 28% and 35% lower on weekends for ROG and NO<sub>x</sub> respectively. However, the changes in emissions result in an increase of the ROG/NO<sub>x</sub> ratio of more than 30% on weekends. STI
  - A survey of business activity showed that business activity declined substantially on weekends (by up to 80%). STI
  - In the urban areas of the SoCAB, surface street traffic volumes (which were dominated by light-duty vehicles) are reduced by about 15% to 30% on weekends and tended to peak around midday rather than during the weekday a.m. and p.m. rush hours. STI
  - Freeway traffic volume information showed that truck and bus activities decreased by up to 80%. On weekends in areas just beyond the urban zones, daily traffic volumes increased somewhat on weekends and tended to peak on Friday and Sunday late afternoons. STI
  - In year 2000, the single largest contributor to emission changes on the weekends is a substantial decline in heavy-duty truck traffic (28% of NO<sub>x</sub> emissions on weekdays and 16% of NO<sub>x</sub> on weekends). STI
  - Major point source NO<sub>x</sub> emissions on Friday, Saturday, and Sunday were 8% to 18% lower, on average, than on Monday through Thursday. STI

- **NO<sub>x</sub> reduction.** Lower NO<sub>x</sub> on weekend mornings leads to higher ozone on weekends because the accumulation of ozone begins earlier on weekends due to less titration of ozone with NO and because of the higher rate of ozone accumulation due to higher VOC/NO<sub>x</sub> ratios.
- Ratio of ambient NO on Saturday and Sunday to midweek are about one-half and one-third, respectively during 0300 to 1500. DRI
- Decrease of ozone precursor concentrations on weekends is proportionately greater for NO than NMHC for all times of the day resulting in higher weekend NMHC/NO<sub>x</sub>. DRI
- A larger fraction of the weekday to weekend differences in ambient NO<sub>x</sub> is attributed to diesel trucks than to gasoline vehicles. Diurnal and weekday variations in NO<sub>x</sub> correlate better with black carbon than with CO or NMHC. DRI
- Ozone formation is VOC-limited throughout the day at the sites examined and peak ozone is less than potential ozone. DRI
- Ozone accumulation begins about 0.5 to 1.5 hours earlier on weekends and rate of ozone accumulation is higher. DRI
- Weekday-weekend differences in the diurnal pattern of NO and ozone are established early in the morning and remains a constant multiplicative constant throughout the daylight hours. DRI

- **NO<sub>x</sub> timing.** NO<sub>x</sub> emitted later in the morning on weekends into an aged photochemical system causes these emissions to produce ozone more efficiently compared to the NO<sub>x</sub> emitted on weekdays.
- On weekends in urban zones, light-duty vehicle traffic peak around midday rather than during the morning and afternoon rush hours.
  - Observed NMHC/NO<sub>x</sub> ratios range from 4-8 from sunrise to peak ozone and ozone formation is VOC-limited throughout this period. Expectation of the NO<sub>x</sub> timing hypothesis is that ozone formation is NO<sub>x</sub> limited on weekend mornings.
  - Weekday-weekend differences in the diurnal pattern of NO and ozone are established early in the morning and remains a constant multiplicative constant throughout the daylight hours.
  - Does not explain the greater decrease in ozone accumulation rates on weekdays during the past two decades nor the decrease in peak ozone relative to its maximum potential ozone on weekdays.

- **Pollutant carryover near the ground.** Greater carryover of precursor emissions due to different vehicle activity on Friday and Saturday evening results in increased rate of ozone formation on weekend mornings.
- Light-duty vehicle traffic is higher on Friday and Saturday nights and lowest on Sunday night.
  - Carryover of NMHC concentration is about 10 to 20 percent higher on weekend mornings relative to midweek. Carryover of NO is 10 to 20 percent lower on Sunday and Monday mornings relative to midweek.
  - Effect on NMHC/NO<sub>x</sub> ratios is small.

- **Pollutant carryover aloft.** Carryover of aged pollutants from aloft on weekend has greater influence on weekend mornings due to lower emissions of NO<sub>x</sub>.
- Pollutant concentrations aloft are significantly lower than in the past. This is inconsistent with strengthening of the weekend ozone effect in the 1990s.
- Weekday-weekend differences in the diurnal pattern of NO and ozone are established early in the morning and remains a constant multiplicative constant throughout the daylight hours. DRI



- **Increased weekend VOC emissions.** Increased VOC emissions from use of lawn and garden equipment, recreational vehicles, backyard barbecues, and household solvents on weekends results in higher weekend ozone concentrations.
- A survey of business activity showed that business activity declined substantially on weekends (by up to 80%). STI
- A survey of residential activity showed that some residential activity increased substantially on weekends, but most activity was independent of day of week. STI
- Ambient apportionments of non-mobile sources to ambient NMHC do not show significant day-of-the-week variations and they have little effect on weekday variations in VOC/NO<sub>x</sub> ratios. DRI

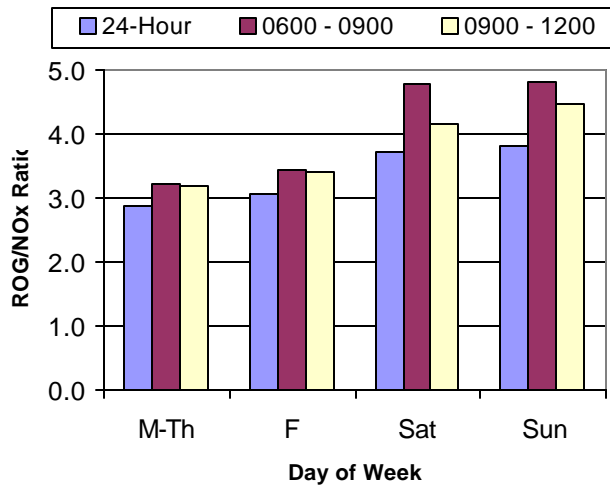
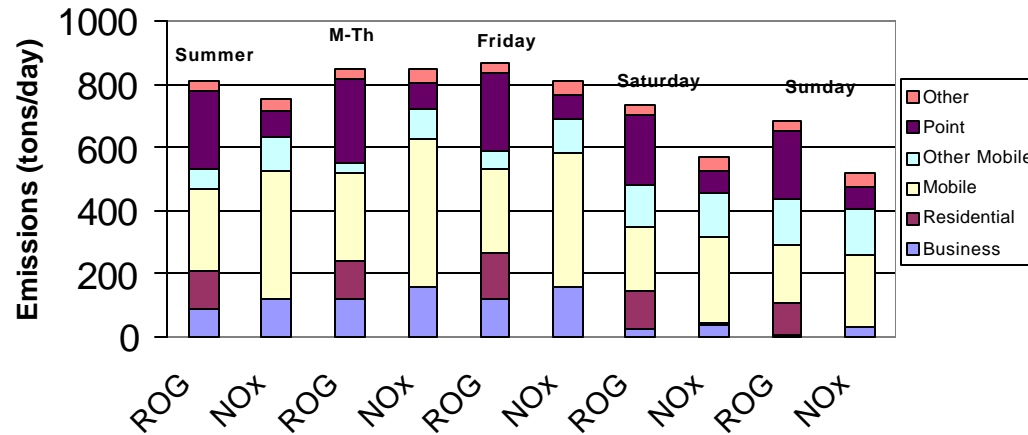
- **Increased photolysis due to decreased emissions of fine particles.** Lower PM concentrations during weekends increase radiation available for photolysis, thus increasing the rate of ozone formation compared to weekdays.
- Photolysis rate parameters have increased historically.
- However, there is no significant weekday differences in photolysis rate parameters.
- Historically the proportion of ozone to potential ozone has not changed on Sundays, but have decreased on weekdays. This is contrary to the historic increase in photolysis rate parameters.

# CONCLUSIONS

Hypotheses	Significance	Confidence Level
1. NOx reduction	Significant	High
2. NOx timing	Insignificant	High
3. Pollutant carryover near the ground	Small	High
4. Pollutant carryover from aloft	Insignificant	Medium
5. Increased weekend VOC emissions	Small to Insignificant	Medium
6. Increased photolysis due to decreased PM	Small to Insignificant	Medium

# Implications

## 2010 Forecasted Emissions



- 2010 forecasted emissions changes result in ROG/NO<sub>x</sub> ratios on weekdays that are comparable to weekends in 2000.

Mean Wednesday  
 $\pm 1$  sigma

Mean Sunday  
 $\pm 1$  sigma

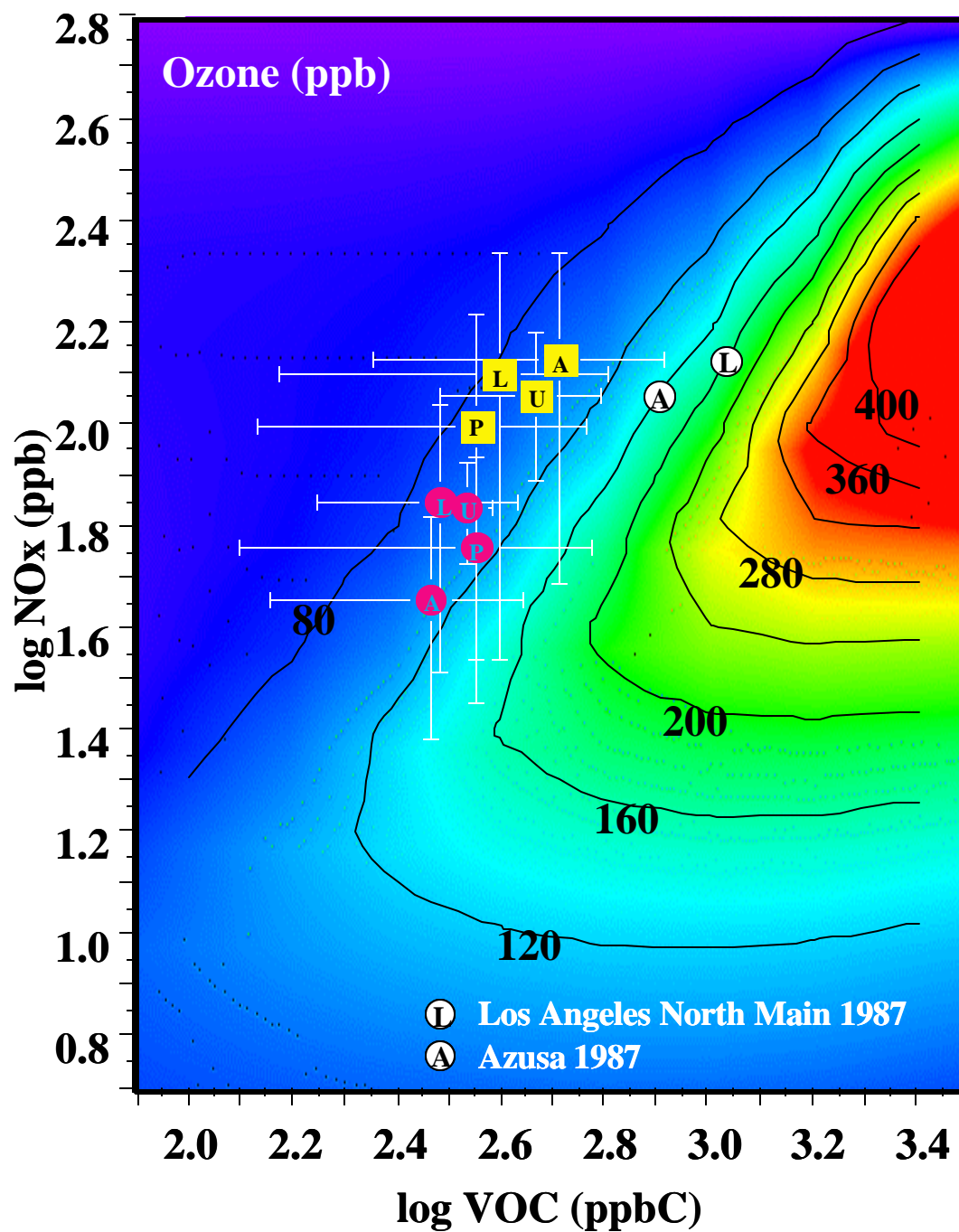
Monitoring Stations

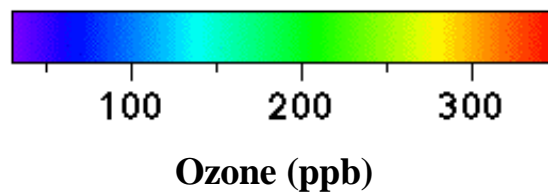
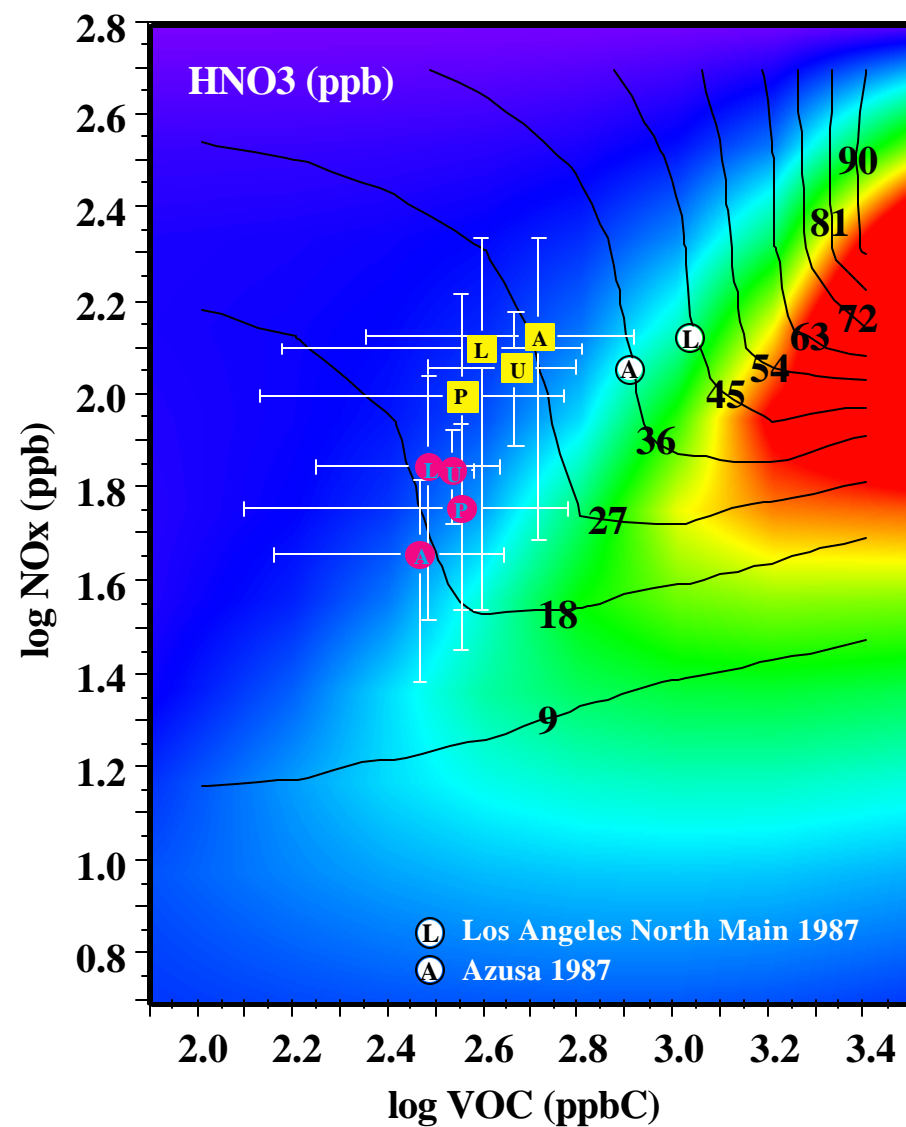
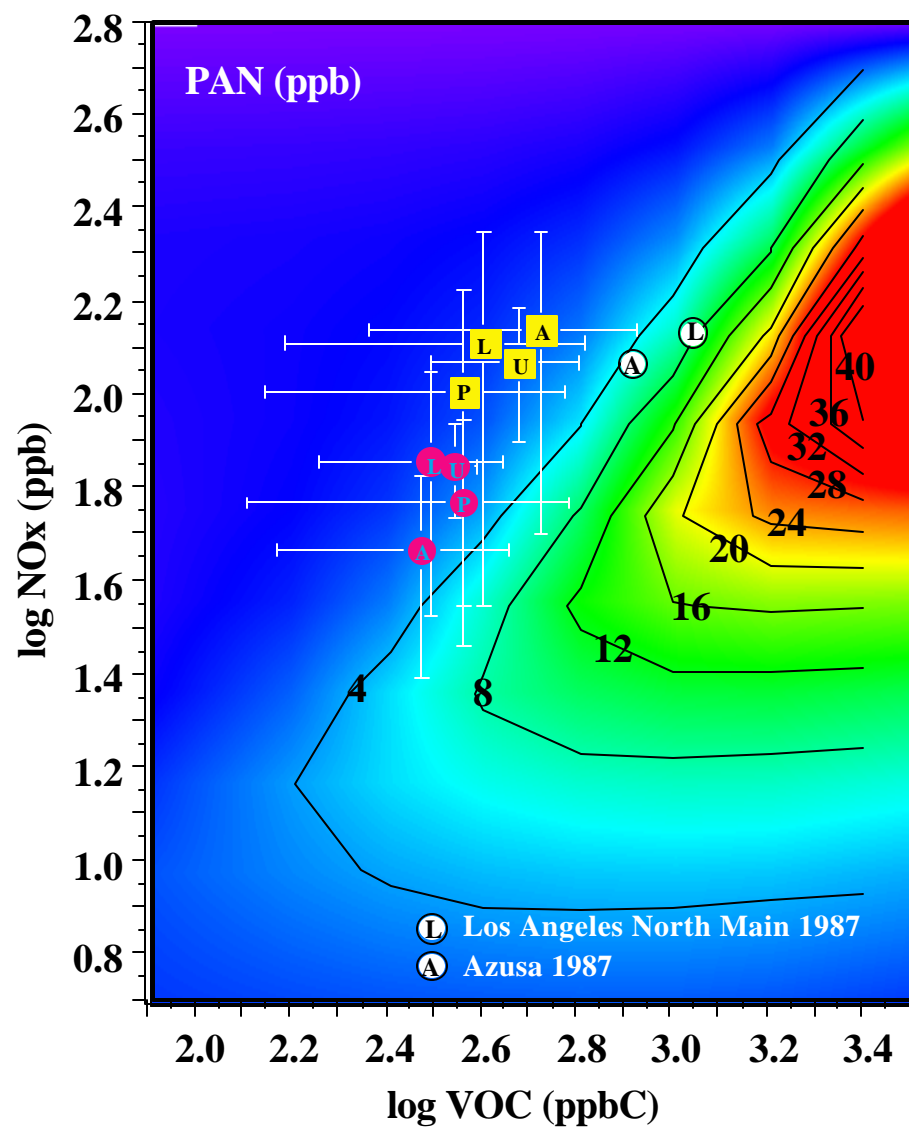
A – Azusa

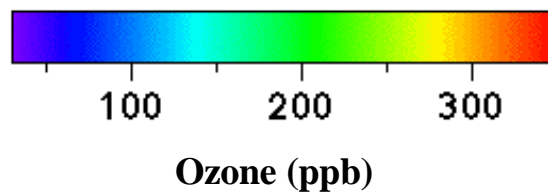
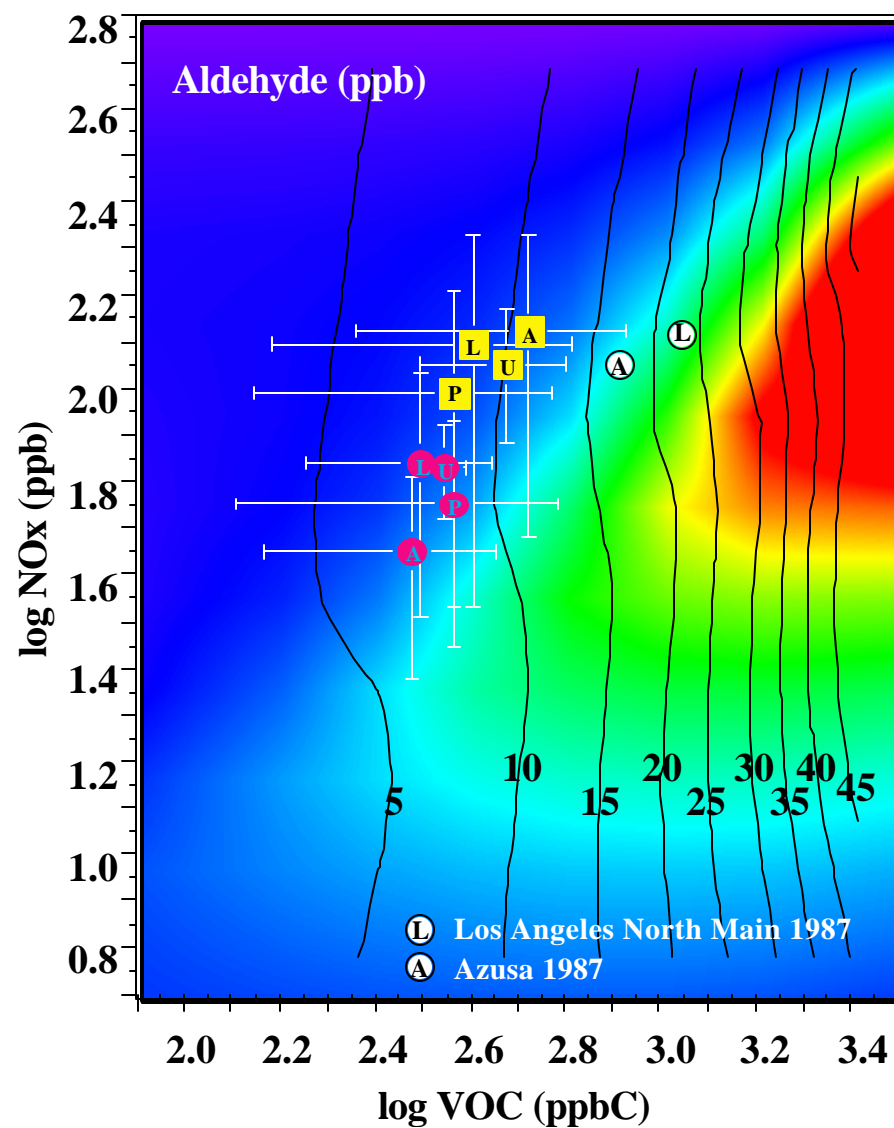
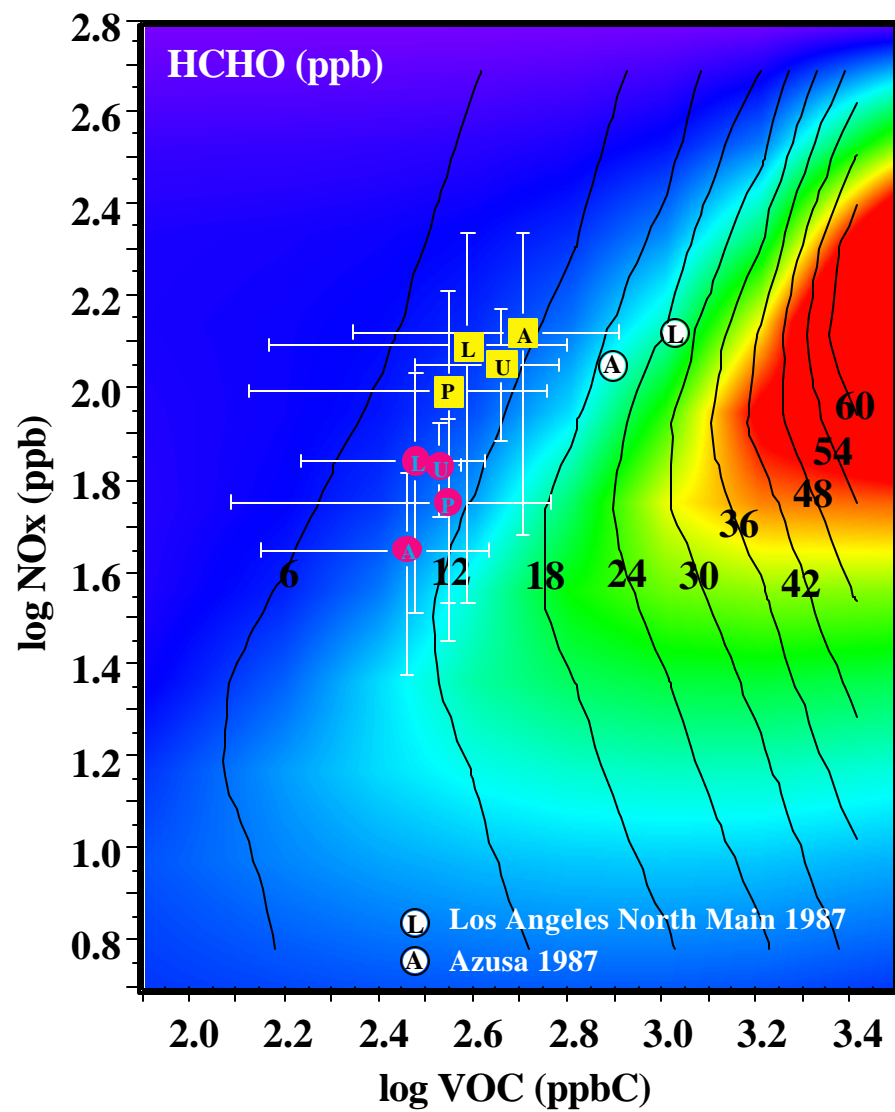
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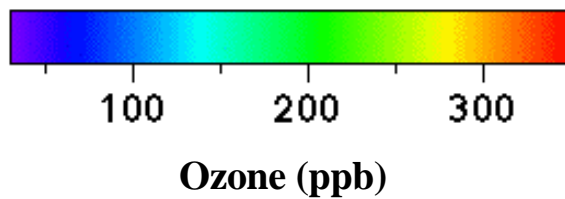
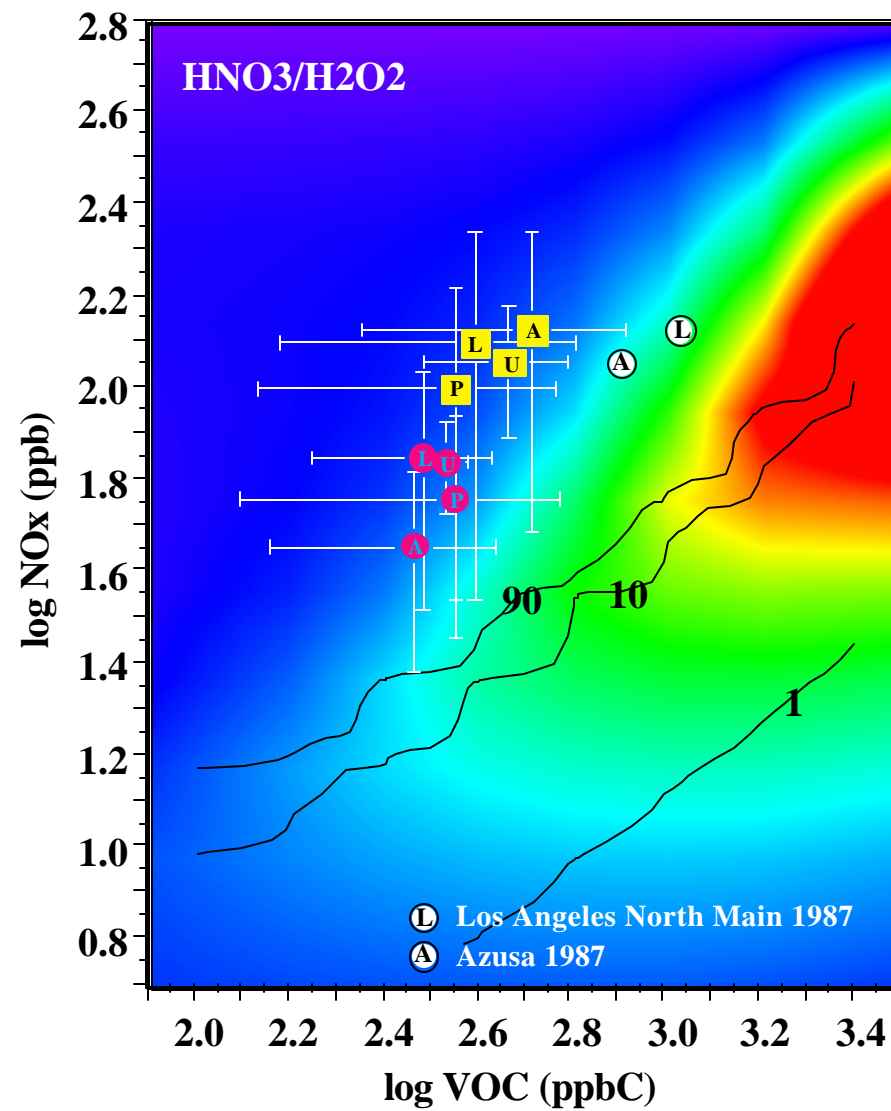
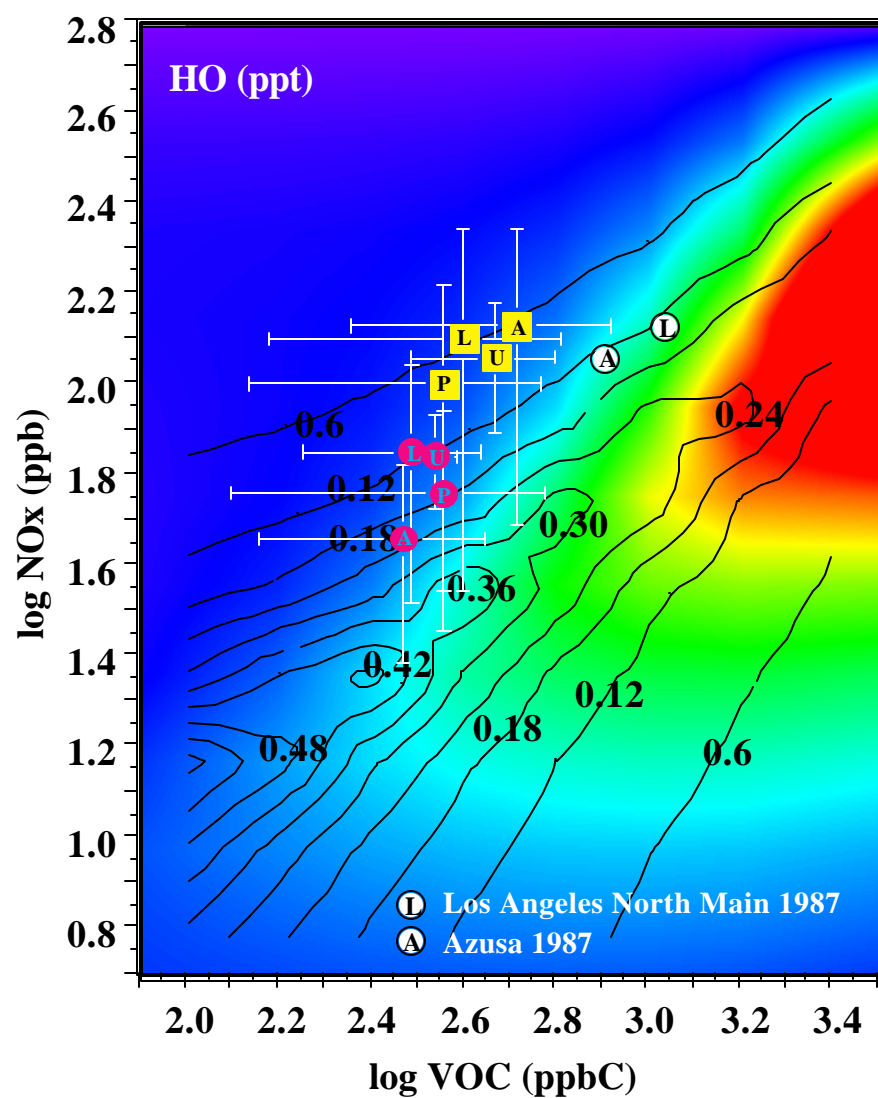
P – Pico Rivera

U – Upland











# RECOMMENDATIONS

- Compare modeling results against the measured temporal and spatial variations of ozone and ozone precursors.
- Evaluation of the accuracy of the temporal and spatial patterns of precursor emissions on weekdays and weekends.
- Perform a series of modeling runs using plausible alternative future emissions inventories for 5, 10 and 15 years into the future and assess direction and sensitivity of projected concentrations of ozone, PAN, nitric acid, particulate nitrate, and formaldehyde.
  - Assess changes in downwind areas where emissions transported from the SoCAB could transition from VOC limited to NO<sub>x</sub>-limited.
  - Assess relative changes to maximum 1-hour and 8-hour ozone levels within the basin.
- Measure species such NO<sub>y</sub>, PAN, HCHO, and speciated hydrocarbons in downwind area to provide corroboration of modeling results.

# Acknowledgments

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## Technical and Logistical Assistance

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- California Air Resources Board
- Bay Area Air Quality Management District